SOIL REMEDIATION GUIDELINES FOR BARITE: ENVIRONMENTAL HEALTH AND HUMAN HEALTH

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Soil Remediation Guidelines for Barite: Environmental and Human Health

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1. INTRODUCTION

The following report compiles and summarizes applicable background information and develops soil remediation guidelines for barite (barium sulphate). Typically, guidelines are developed for trace elements, rather than for inorganic compounds of the elements. However, a specific guideline for barite is justified and required on account of (i) the very low solubility and availability of barite in comparison with the soluble barium compounds that were used to develop the CCME (1999 and updates) barium soil quality guideline, and (ii) the ubiquitous presence of barite in the soil of former oil and gas drilling sites owing to its use as a major component of oilfield drilling muds.

The barite soil remediation guidelines developed herein follow Alberta Environment (2009) protocols wherever applicable and appropriate, and only deviate from these protocols where dictated by particular issues relevant to barite.

Appendices referenced in this document may be found in a separate document: *Technical Appendices for Barite Soil Remediation Guidelines*, also available on the Alberta Environment Website.

Note that guideline values in this document are presented to "1.5 significant figures" which in the context of this report means the calculated values are rounded to 1 significant figure with a "5" or a "0" in the second figure.

1.1 Changes from Previous Version

This document supersedes the AENV (2004) barite guideline document. The main changes in the current document from the previous version are as follows:

1. The human tolerable daily intake for barium has been updated to reflect new findings by the US EPA.
2. The daily threshold effect dose (DTED, toxicological reference value for mammalian wildlife and livestock) for barium has been updated to reflect new findings by the US EPA.
3. A more detailed review and discussion of the issues affecting barite bioavailability has been added.
4. The section on analytical methods for barium in soil has been revised to reflect new requirements for analysis of barite-barium.
5. A requirement has been added that the barite guidelines can only be used where measured barium concentrations are based on a true total barium analysis. True total barium must be measured by Fusion ICP or Fusion XRF (see Section 9.1.2).

6. Guideline values are now presented to 1.5 significant figures.
7. New appendices have been added to support i) the discussions of appropriate analytical methods for barium in soil and ii) an appropriate value to use for the bioavailability of barite.

2. BACKGROUND INFORMATION

Barite ($BaSO_4$; CAS No. 7727-43-7) is a mineral in the anhydrous sulphate series and is one of the most common naturally occurring forms of barium United States Environmental Protection Agency, (US EPA, 2005a). Synonyms of barite include barium sulphate, barytes, heavy spar, and blanc fixe World Health Organization, (WHO, 2001). Barite is often found as underground ore deposits and is commercially mined in China, USA, India, Morocco, Kazakstan, Mexico, Germany, Iran, Turkey, Canada, and other countries (NRC, 2007). The physical and chemical properties of barite make it useful in a variety of industrial and commercial applications.

2.1 Physical and Chemical Properties

The physical and chemical properties of barite are summarized in Table 1. Barite exists as colourless to white, orthorhombic dipyramidal powder or crystals (WHO, 2001). Impurities associated with barite include aluminum oxide, arsenic, barium, calcium, copper, fluorine, iron (III) oxide, lead, manganese, silica, strontium sulphate, zinc (WHO, 2001), cadmium (Nelson *et al.*, 1984), mercury (Creselius, 2007), or radium (Phillips *et al.*, 2001).

Barite is brittle with a hardness of 3 to 3.5 on the Mohs scale (CRC, 1983) and has a specific gravity of 4.5, which is heavy for translucent minerals (CRC, 1983). Barite is practically insoluble in water (US EPA, 2005a), organic solvents (CEPA, 2002), and weak acids due to the very strong affinity of barium (Ba^{2+}) for sulphate (SO_4^{2-}) ions (US EPA, 1997).

2.2 Analytical Methods

No published procedures were found for the quantitative measurement of barite in soil, water, or air. Generally, published analytical methods measure the concentration of barium and do not provide information on the speciation of barium compounds (WHO, 2001).

The following sections refer to quantitative analytical methods for barium rather than barite.

2.2.1 Soil

Soil methods are generally also applicable to sediment and oilfield waste. Typically, methods to measure barium concentrations in soil samples involve an extraction or fusion process followed by analysis of the digest. A range of different methodologies has been used to generate a digest. The methods vary in the amount of barium that they extract, and fall into three general groups (given names here for convenience only).

Fusion Methods

These methods are in common use in the mineralogical analysis of rock samples, but have previously not been widely used in the analysis of environmental samples. Techniques rely on fusing the sample mixed with a flux at high temperatures (1,000 to 1,200°C) in a crucible. Commonly used fluxes include sodium carbonate (Na_2CO_3), potassium carbonate (K_2CO_3), borax ($Na_2B_4O_7$), lithium tetraborate ($Li_2B_4O_7$), and lithium metaborate ($LiBO_2$). ASTM (2008) provides a standard method based on $LiBO_2$. A range of fusion methods are discussed in Johnson and Maxwell (1989). ICP and XRF techniques have each been used to analyze barium in the digest. Fusion methods typically extract essentially all the barium in a sample.

Strong Acid Methods

These have been the methods traditionally used to analyze environmental soil samples for metals. However, recent work (BCLQAAC, 2007, reproduced in Appendix I, and Dodd et al., 2007, reproduced in Appendix II) has shown that these methods are often inadequate to quantify total barium in environmental samples containing barite, and are limited by the solubility of barite in the acid. In some cases, standard strong acid methods recovered as little as 13% of the barite-barium in a soil sample (BCLQAAC, 2007).

Strong acid methods typically involve sample dissolution using a single strong acid or a mixture of strong acids (e.g., HNO_3, HCl) to dissolve the sample at an acid:sample ratio typically between 5:1 and 20:1. Other elements such as the addition of hydrogen peroxide (H_2O_2) or microwave heating may be included. Standard methods for strong acid digestion include US EPA (2008) Methods 3050B, 3051A, and 3052, and the British Columbia "Strong Acid Leachate Method" (SALM).

One significant variation on the strong acid methods is the "Louisiana" Method. The Louisiana Department of Natural Resources (LDNR) has developed an extraction method for barium specifically for use on oilfield exploration and production waste. The LDNR (1988) method uses HNO_3 at a lower concentration than the US EPA (2008) methods, but at a higher acid to sample ratio (LDNR, 1988). Deuel and Holliday (1998) found that this method provided significantly better recovery of barium from barite than the US EPA methods. The LDNR method has been revised since the Deuel and Holliday (1990) work (LDNR, 2001a).

Extractable Methods

These methods extract the sample with a neutral solvent and recover principally barium adsorbed to soil particles, present as soluble salts, or bound to organic material. These methods typically recover a much smaller proportion of barium than either fusion or strong acid methods, but have been used to estimate the amount of barium that might be available to plants and soil invertebrates. Deeley and Canter (1986) used H_2O, KNO_3, and EDTA, to extract barium from drilling fluids. They found that the amount of barium extracted varied between different drilling wastes and that KNO_3 and EDTA were more effective than H_2O at extracting barium. The method developed for measuring extractable barium in Alberta is based on an extraction with 0.1M $CaCl_2$. Details are provided in Appendix III. Note that the British Columbia Ministry of the Environment has also developed a similar method for extractable barium, with the primary difference being the use of 1 M, rather than 0.1 M $CaCl_2$ as the extractant.

Analytical Methods

The digest produced by the above methods can be analyzed by one or more of the following techniques: atomic absorption spectrophotometry (AAS), flame atomic absorption spectrophotometry (FLAA), graphite-furnace atomic absorption spectrophotometry (GFAA), inductively coupled plasma - optical emission spectrometry (ICP-OES), inductively coupled plasma mass spectrometry (ICP-MS), or x-ray fluorescence (XRF). US EPA (2008) Methods include 6010B and 6020. Environment Canada (1999) states that US EPA Method 6010 is the recommended analytical measurement for barium in soil.

Required Analytical Methods for Alberta Barite Guidelines

The Alberta barite-barium guidelines are applicable only to sites contaminated by barite. Extractable barium, measured after extraction with 0.1M $CaCl_2$, must be measured and compared to the appropriate guideline in Table 6. If the analytical results fall on or below the extractable barium guideline, the site meets the conditions of a barite-site and the true total barite-barium guidelines can be applied

The true total barite-barium guidelines in this document were developed to be compared to true total barium concentrations. Thus, barium must be characterized using an analytical technique that is capable of measuring true total barium. Soil samples taken for comparison to the true total barite-barium guidelines must be analyzed by fusion techniques (e.g., fusion-ICP or fusion-XRF).

Note that fusion methods typically use a very small sample size. Consideration should be given to either thorough sample homogenization and/or analyzing multiple replicates from a sample container to reduce random elements introduced by sample heterogeneity.

2.2.2 Water

US EPA (2008) recommends that the digestion of water and other aqueous samples follow Methods 3005A, 3010A, 3015, or 3020. These methods are based on acid digestion or microwave-assisted acid digestion for analysis of total recoverable, dissolved, or total metals (including barium). These digestion methods are suitable preparation for analysis by US EPA (2008) Methods 7080A and/or 7081 using FLAA, GFAA, ICP-AES, or ICP-MS.

Two environmental analytical laboratories in Alberta use US EPA Methods 3005A, 3015 or modifications thereof for digestion, depending on the solid content of the aqueous sample. Analyses are conducted using ICP-AES or ICP-MS.

2.2.3 Air

Methods to measure barium compounds in air include an ashing procedure prior to a flame atomic absorption method (NIOSH, 1987 cited in WHO, 2001) or gravimetric assessment of respirable dust samples (OSHA, 1990 cited in WHO, 2001). Atomic absorption spectroscopy (AAS) has also been used to measure barium in air (Miner, 1969 cited in ATSDR, 1992).

2.3 Production and Uses in Canada

In Canada, barite is commercially produced from mines in British Columbia, Newfoundland and Labrador, Nova Scotia, and Ontario (NRC, 2007). Preliminary estimates of revenue generated from barite production in 2006 were $596,000 for Nova Scotia, $2,500,000 for British Columbia and $1,500,000 for Ontario (NRC, 2006). Approximately 2% of the barite produced globally was from Canadian mines (USGS, 2001) and approximately 7.3% of global barite reserves are located in Canada (USGS, 2001) in 1999 and 2000. China has recently replaced the US as Canada's largest external supplier of barite, while most of the barite exported from Canada typically goes to the US (NRC, 2007).

In 2006, approximately 24,936 tonnes of barite was used in Canada (NRC, 2006). Up to 90% of the barite produced is used as a weighting agent in oil and gas drilling muds. Drilling muds are pumped down into the borehole during the drilling of oil and gas wells to lubricate and cool the drill bit, float cuttings out, seal rock strata that are porous, and apply hydrostatic pressure to prevent water from filling the borehole (Nelson *et al.*, 1984). Barite is an excellent drilling mud additive because it is soft, easily crushed and milled, virtually chemically inert, has no magnetic effects, is not abrasive, and has a high specific gravity that can withstand high downhole pressure (WHO, 2001).

The following industries also use barite:

- barium compound manufacturing (barite is used as a source of barium);
- pharmaceutical industry (purified barite, which is radio-opaque, is administered in a "barium milkshake" or enema prior to gastrointestinal x-rays);
- the manufacturing of products including paint, optical glass, ink, linoleum;
- sugar refining;
- television and computer screen manufacturing (barite is used in the faceplates and funnelglass of cathode-ray tubes);
- metal casting (barite is used in the mold-release compounds);
- vehicle manufacturing (barite is used in the friction products for brake and clutch pads);
- food manufacturing (barite can be used as a forming agent);
- paper and rubber manufacturing (barite is used as a filler or a weighting agent);
- heavy concrete production (barite is used as a radioactive shield);
- firework production (barite is used to make the colour green); and,
- pond repair (barite is used to stop leaks in lined ponds that cannot be drained).

The above list was generated using information from the following sources: ADMMR, 2001; USGS, 2001; CEPA, 2003; Williams, 2003; and Code of Federal Regulations (2008).

2.4 Levels in the Canadian Environment

Barite is a naturally occurring mineral in the Canadian environment, but anthropogenic sources also release barite to the environment. Most quantitative analytical methods measure total barium concentrations in various media; thus, little information was available on barite concentrations in the Canadian environment. The following sections qualitatively discuss barite levels in the Canadian environment.

2.4.1 Atmosphere

Barite is not volatile (Quantum Chemicals, 2005) but may be present in the atmosphere as dust and suspended particles (Environment Canada, 1999). Barite and barium carbonate are the most likely forms of barium found in atmospheric particulate matter (WHO, 2001).

Atmospheric barite may be emitted during anthropogenic activities or as dust originating from barite-containing soil or mining activities (WHO, 2001). Although barite is present in the air where dust levels are naturally high (WHO, 1990 cited in Environment Canada, 1999), the primary source of barium in the atmosphere is from industrial activities (US EPA, 2005a). In 1976, the mining and processing of barite ore released approximately 3,200 tonnes of barite to the atmosphere. Fugitive dusts from the use of barite in drilling activities released an additional 100 tonnes of barite (WHO, 1990 cited in Environment Canada, 1999). Barite is also emitted to the atmosphere in the exhaust of diesel-powered vehicles. Pierson *et al.* (1981

cited in Environment Canada, 1999) reported approximately 95% of the barium added to diesel fuel was emitted as barite in exhaust.

No information on barite concentrations in ambient air was found.

2.4.2 Indoor Air

Although a proportion of airborne house dust likely contains barite, studies evaluating the concentration of barite in indoor air have concentrated on factory situations. In factories where barite is added to mixing hoppers, barite concentrations of 3.5 to 9.1 mg/m^3 (8-h time-weighted-average) were measured in air. Barite levels in air ranged from 1.3 to 3.7 mg/m^3 in factories where barite ore is processed and from 1 to 3.5 mg/m^3 in factories where plastics and coatings are formulated (WHO, 2001).

2.4.3 Soil

Barite occurs naturally in soil and is precipitated into geological faults when soluble barium minerals (resulting from limestone, feldspar, and/or shale deposit weathering) encounter sulphate solution (WHO, 1990 cited in Environment Canada, 1999). Barite deposits are commonly associated with quartz, fluorspar, calcite, and metallic sulphides and may be present at the soil surface (in outcrops, hillsides, or soil concretions) or deep below the earth's surface (ADMMR, 2001; WHO, 2001). The majority of barite is found in sedimentary formations, as nodules resulting from the weathering of barite-rich sediments, in veins in limestone and sandstone, or in beds (WHO, 2001; Deuel, 2003).

CCME (1999 and updates) provides information on the concentration of barium in uncontaminated Canadian soils. Uncontaminated surface soils (n = 1,244) from Quebec had a mean barium concentration of 62 mg/kg. Uncontaminated soils from rural locations in Ontario (n = 101) had a mean barium concentration of 72 mg/kg. All these samples were analyzed using inductively coupled plasma (ICP) or atomic absorption spectrometry (AAS) following HNO_3/HCl digestion. Data from the Prairie Provinces were available, but had been subjected to a much more aggressive digestion technique ($HF/HClO_4/HNO_3$). This digestion technique can release barium from mineral grains, and accordingly the measured barium concentrations were higher (mean = 662 mg/kg; n = 1,273), but could not be compared with standard environmental analyses (which use an HNO_3/HCl or similar digestion), and accordingly were not used here. The mean of the Quebec and Ontario data was 67 mg/kg.

Measured barium concentrations from two background samples from a clay till soil at a site in southwest Alberta were 281 mg/kg and 224 mg/kg, respectively (ESG, 2003b). This site was also the source of the soil used in the studies reported in Appendices IV, V, VI, and VII.

The mean barium concentration in 1,128 samples of ambient soil from Alberta was 325 mg/kg, based on strong acid digest methods. (Alberta Environment database, Gordon Dinwoodie, *pers. comm*). This value is used here as a reference background soil concentration.

The disposal of waste drilling muds containing barite is the primary anthropogenic input of barite to soil systems (CEPA, 2002). Once a well is completed, drilling muds are often incorporated into the surface soil of the site or placed in lined or unlined earthen pits ("sumps") on-site, and subsequently mixed, buried and covered with subsoil. Water-based and/or hydrocarbon-based (i.e., "invert') drilling muds often contain barite, bentonite, and other additives (Nelson *et al.*, 1984). The barite concentration in drilling mud used for deep wells may exceed 100,000 mg/kg (Deuel, 2003) and was reported for three sources of barite to range from 429,000 to 509,000 mg/kg (Nelson *et al.*, 1984). The trace elements arsenic, cadmium, chromium, copper, lead, mercury, nickel, and/or zinc were also present in the barite or drill cuttings (Nelson *et al.*, 1984).

Barite supplied by Dynatec Corp. (one of the two main suppliers of barite to the Canadian oilfield), between 1992 and the present, has typically contained between 87% and 94% barium sulphate, with the majority of the balance being silica (information supplied by Dynatec Corp. to Chris Meloche, Chevron Canada Resources, 12 February 2003). Maximum levels of trace metals, based on the information supplied, were as follows. Only data for metals for which has soil remediation guidelines are included.

- Arsenic 9 ppm
- Cadmium 0.5 ppm
- Chromium 10 ppm
- Copper 180 ppm
- Lead 6 ppm
- Mercury 5 ppb
- Nickel 10 ppm
- Selenium 0.1 ppm
- Vanadium 6 ppm
- Zinc 16 ppm

All these values are below the CCME (1999 and updates) agricultural guidelines, except for copper (guideline = 63 mg/kg).

Soil/drilling fluid mixtures collected from drilling sumps and flare pits throughout Alberta often contain total barium concentrations in excess of the CCME (1999 and updates) barium guidelines (750 mg/kg for agricultural land use and 2,000 mg/kg for commercial/industrial

land use). Soil and soil/drilling fluid samples collected from 5 flare pits, 7 drilling sumps, and 2 oilfield landfarm areas, yielded elevated total barium concentrations up to 20,700 mg/kg. The majority of soil/drilling fluid samples from sumps and flare pits contain barium at concentrations between 1,000 and 4,000 mg/kg (Komex International Ltd, unpublished data).

2.4.4 Water and Sediments

The majority of barium in sediments is in the form of barite (Environment Canada, 1999). Barite may be present in the water column as a suspended solid, but is usually removed by sedimentation (US EPA, 1997).

No information on barite levels in sediments of Canadian water bodies was found.

2.4.5 Drinking Water

Information regarding the barite content of drinking water in Canada was not found. However, treatment systems typically remove suspended matter (including barite) from drinking water. Barite in water can dissolve to release low concentrations of barium and sulphate ions. Health Canada (1990) provides a review of barium concentrations in raw, treated, and distributed drinking water in Canada and CCME (1999 and updates) lists barium concentrations in raw water, some Canadian rivers, sediments, and groundwater. The distribution of dissolved barium in drinking water is beyond the scope of the current report.

2.4.6 Biota

Plants and animal tissues are not expected to absorb high concentrations of barite due to its very low solubility; however, barite may be deposited onto plant leaves or be present in the respiratory or digestive systems of animals. Under certain conditions, the solubilization of barite may occur, making barium available to organisms (these processes are discussed in Section 3). Freeman and Deuel (1984) studied the impacts of land treating drilling wastes (containing barite) in wetland areas and reported the tissue from plants growing on closed drilling waste pits yielded up to 4.6 times more barium than the tissue of plants grown in background soil. Deuel (2003) also reported that plants grown in wetland areas where barite-rich oilfield waste had been deposited in pits contained average barium concentrations of 541 mg/kg, whereas plants grown in background wetland soils contained average barium concentrations of 304 mg/kg. In contrast, Nelson *et al.* (1984) conducted a greenhouse study and found barium levels in plants grown on non-saturated background and soil-drilling mud mixtures to be similar.

2.4.7 Oilfield Drilling Muds

The Alberta Research Council (ARC, 1992) conducted a study of the trace metal content of samples of 651 drilling muds. The mean measured total barium concentration in the solids from the drilling muds was 322 mg/kg, though the maximum measured value was much higher at 23,400 mg/kg. On average, invert muds (*i.e.*, diesel-based muds) had a higher total barium content than water-based muds. The analytical method used to determine the total barium concentrations involved an aggressive digestion technique using a mixture of HHO_3, HCl, and HF in a Teflon bomb in a microwave oven.

ARC (1992) also analyzed saturated paste extracts to investigate the concentrations of soluble trace metals present in drilling muds. The mean barium concentration in saturated pastes from all 651 muds was 0.32 mg/L, while the maximum was 11.4 mg/L. On average, invert muds had a higher saturated paste barium content than water-based muds.

2.4.8 Other

Information on barite or barium (as barite) concentrations in biota used as human food, commercial food, or breast milk was not found. Barite is sometimes used in food production and has been ruled safe for use in the manufacturing of resinous and polymeric coatings in contact with food (Code of Federal Regulations, 2008).

2.5 Existing Guidelines and Criteria in Various Media

No Canadian guidelines that regulate barite levels in air, water, sediment, or soil have been developed. Although risk-based guidelines for total barium concentrations in drinking water and soil exist (CCME, 1999 and updates), they are not considered applicable to barite as they were developed using literature on soluble barium salts (*e.g.*, barium chloride). Soluble forms of barium have very different fate, transport, and toxicological behaviours than those of barite.

2.5.1 Air

The US Occupational Safety and Health Administration (OSHA) workplace permissible exposure limits for barite in air are 15 mg/m^3 for total dust and 5 mg/m^3 for the respirable fraction (OSHA, 2003). The National Institute for Occupational Safety and Health (NIOSH, 1989) recommended exposure limits for barite in air are 10 mg/m^3 for total dust and 5 mg/m^3 for the respirable fraction. Both OSHA and NIOSH limits are time-weighted averages for an 8-h period.

US EPA (2008) Region 9 derived preliminary remediation goals (PRGs) for sites contaminated with barium and/or barium compounds. The risk-based PRG calculated for ambient air is 0.52 $\mu g/m^3$ (US EPA, 2008).

2.5.2 Water and Sediments

No barite guidelines for water or sediment were found.

Barium guidelines for drinking water of 1 mg/L were developed by CCME (1999 and updates) and Health Canada (1990). The US EPA guideline for barium in drinking water is 2 mg/L (US EPA, 2003).

2.5.3 Soil

Louisiana developed criteria for total barium levels in exploration and production wastes. Louisiana Statewide Order 29-B (amended) provided a total barium criterion of 20,000 mg/kg for the closure of pits, containing residual oil and gas exploration and production wastes, located on submerged or elevated wetland sites (LDNR, 2001b). Guidelines of 40,000 mg/kg (LDNR, 2001b) and 100,000 mg/kg (LDNR, 1990 cited in API, 1995) were provided for upland land resources and commercial landfill operations, respectively.

Following the study of many more Louisiana sites, Deuel (2003) recommended a barium guideline of 100,000 ppm for the passive closure of sites containing residual oil and gas exploration and production wastes. Deuel (2003) also suggested that the need for a barium guideline was negated for passive closure sites where sufficient agricultural grade gypsum is topically applied as a sulphate source to precipitate the barium ions into barite.

In 1995, the American Petroleum Institute (API) derived risk-based guidelines for barium in exploration and production wastes. A maximum barium concentration of 180,000 mg/kg (measured using the LDNR extraction method for "true total barium") was determined for soil (API, 1995).

US EPA (2008) Region 9 PRGs for sites contaminated with barium and/or barium compounds are 15,000 mg/kg for residential soil and 190,000 mg/kg for industrial soil. Soil barium concentrations of 82 and 300 mg/kg were calculated for the protection of drinking water Maximum Concentration Limits (MCL) or systemic toxicity-based limits respectively on the assumption that no dilution or attenuation in the soil occurs (US EPA, 2008).

CCME (1999 and updates) provides soil quality guidelines for barium that are based on soluble barium compounds. CCME (1999 and updates) guidelines for agricultural,

residential/parkland, commercial, and industrial land uses are 750 mg/kg, 500 mg/kg, 2,000 mg/kg, and 2,000 mg/kg, respectively.

3. ENVIRONMENTAL FATE AND BEHAVIOR

Barite is not very mobile or bioavailable under most atmospheric, water, or soil conditions and does not undergo photolysis, abiotic, or biotic oxidation to yield barium ions (US EPA, 1991). Information on the environmental fate and behaviour of barite or barium (as barite) is limited because the barium cycle has not been investigated (Baldi *et al.*, 1996). The following sections provide a limited discussion on the environmental fate and behaviour of barite in the environment.

3.1 Atmosphere

Most anthropogenic sources of barium emissions release barium (including barite) in particulate form. Atmospheric barium is not widely dispersed (US EPA, 1997). Although some smaller barium-containing particles may have a residence time in the atmosphere up to a few days, the majority of particles are greater than 10 µm in size and will quickly settle back to land or water (WHO, 2001). The residence time of barium-containing particulates in air is a function of barium speciation, the chemical nature of the particulate, and environmental factors (*e.g.*, rainfall). Barium is deposited to land and water through wet and dry deposition (US EPA, 1997).

3.2 Water and Sediments

Barite solubility is very low in water due to the strong affinity of barium ions for sulphate ions (US EPA, 1991). Because barite readily forms and precipitates out of solution, barium ion availability in water is usually inversely related to the sulphate concentration (WHO, 2001). US EPA (1997) states that natural waters containing barium usually contain enough sulphate and carbonate to precipitate barite and/or barium carbonate. Once formed, barite is very sparingly soluble under neutral pH and oxidized conditions (Carbonell *et al.*, 1999). Deeley and Canter (1986) completed chemical analyses on the aqueous phase of a drilling mud pit and found that while high levels of total barium were present in the sediments, much lower aqueous phase concentrations of barium were present. Barium formed compounds that were insoluble over a wide range of pH values.

Deuel (2003) reports the soluble barium released from barite in water increased from 1.38 mg/L (with 1,000 mg barite/L) to 24.9 mg/L (with 1,000 mg barite and 30,000 mg NaCl/L) with the addition of salts. Subsequent addition of 10,000 mg gypsum/L to the barite/salt

mixture reduced the soluble barium concentration in water to 0.02 mg/L. The low availability of barium from barite is a function of its low solubility and the high affinity of barium ion for the sulphate ion (US EPA, 1991).

Barite suspended in the water column usually deposits onto the sediments (US EPA, 1997). Suspended barite may be transported for great distances if high flow and low sedimentation rates are present (WHO, 2001).

In anaerobic environments under low sulphate conditions, anaerobic bacteria can enhance barite solubility in aqueous environments and potentially result in increased concentrations of dissolved barium. In nature, anaerobic, sulphur-poor aquatic environments exist, but are often present in northern glaciated regions in isolated water bodies (*i.e.*, not connected to flowing surface and groundwater). These remote aquatic systems are unlikely to release barium ions at concentrations that are ecologically significant (US EPA, 1997).

As barite is dissolved under certain pH, temperature, and dissolved sulphate level conditions, sulphur-reducing bacteria utilise the sulphate, disrupt the dissolved / solid equilibrium and cause more barite to be dissolved. Microbial solubilization of barite in anaerobic environments can release barium ions from barite at concentrations greater than expected based on barite solubility (US EPA, 1997; McCready *et al.*, 1980) and potentially release trace elements co-precipitated in the barite (*e.g.*, arsenic). Some anaerobic microorganisms use dissolved sulphate as an electron acceptor for anaerobic respiration and thus reduce sulphate to sulphite. Barium ions do not form stable compounds with sulphite ions, and accordingly dissolved barium concentrations may increase (US EPA, 1991). Soluble barium, released from barite via the process described above can form other barium compounds (*e.g.*, $BaCO_3$, BaS) (Baldi, *et al.*, 1996), which may be more bioavailable to aquatic organisms than barite itself. McCready *et al.* (1980) found that sterilised sediments, containing no microorganisms, released minimal barium.

Under reducing conditions, barite solubilization has been reported by Huck *et al.* (1989) and Fedorak *et al.* (1986) who investigated the bacterial reduction of barium/radium sulphate sludges in mine tailing pond sediments and the subsequent release of soluble barium to the overlying water. Fedorak *et al.* (1986) found the sulphate-reducing activities of microorganisms in radium mining sludges to be carbon limited and Phillips *et al.* (2001) reported that barium ion release in three oilfield wastes was dependant on the respiration rates of sulphate-reducing bacteria. Carbonell *et al.* (1999) also demonstrated the release of soluble barium from barite in sediments under low pH and highly anaerobic conditions and McCready *et al.* (1980) found soluble barium release from barite in sediments was dependent on pH and the sulphate concentration. The greatest amounts of barium were released at high and low pH (McCready *et al.*, 1980). *Desulfovibrio vulgaris* was identified as the sulphate-reducing organism responsible for metabolising barite in radium mine sludge under neutral

pH conditions in anaerobic sediments by McCready and Krouse (1980, cited in McCready *et al.*, 1980) and *Desulfovibrio desulfuricans* was shown to release soluble barium from barite in sewage sludge under anaerobic conditions (Baldi *et al.*, 1996).

While barite solubilization under reducing conditions has been demonstrated, the resulting concentrations of dissolved barium may be lower than expected based on stoichiometry. Phillips *et al.* (2001) reported that while sulphate-reducing bacteria released soluble barium from barite in three different oil-field materials, Ba^{2+} release was not stoichiometric with sulphide production and released less than 0.1% of the barium present in barite. Baldi *et al.* (1996) reported that the concentration of soluble barium released (1.2 mg Ba/L was measured) was well below the concentration expected based on the amount of H_2S evolved (109 mg Ba/L was expected). McCready *et al.* (1980) also found precipitated barite becomes less soluble with age.

3.3 Soil

Barite in soil has very low mobility due to its insolubility (US EPA, 1997) and inability to form soluble complexes with humic and fulvic matter (US EPA, 1984 cited in WHO, 2001). Due to the strong affinity of barium ions for sulphate, the amount of barium present in well-aerated, neutral soils is dependant on sulphate availability (US EPA, 1991). Under non-saturated conditions and natural fluctuations in pH, barite solubility in soil is unlikely to increase (Deeley and Canter, 1986).

Decreased pH, anaerobic conditions, reduced reduction-oxidation potential, elevated chloride or dissolved salt concentrations, and low sulphate concentrations can all result in the solubilization of barite and increased concentrations of dissolved barium in soil (US EPA, 1991; Branch *et al.*, 1990). Deeley (1984; cited in US EPA, 1991) demonstrated that barite can be converted to a soluble barium salt [salt was not specified] in landfills under certain pH and ionic strength conditions. However, soil pH conditions low enough to cause barite solubilization (*i.e.*, pH < 4) are unlikely to occur in oilfield drilling sumps as drilling muds and/or clay textured subsoil (i.e., "mineral soil") have a large neutralizing capacity. Deeley and Canter (1986) concluded that pH changes in the natural environment would not be sufficient to result in the release of soluble barium from barite. Deuel and Freeman (1989) also concluded that in the natural environment, barite poses no risk under oxidative conditions. Redox conditions sufficiently low to solubilize barite (*i.e.*, -200 to -240 mV), are rarely found in mineral soils (API, 1995).

A study by Deuel and Freeman (1989) found that barite in drilling mud remains in the solid phase even after being pumped downhole and subjected to heat and alkaline conditions during drilling. API (1995) stated that in many cases, the addition of barite to soil in the form of

drilling fluids may have no effect on barium concentrations in soil solution. Deuel and Holliday (1998) concluded that the majority of barium present in drilling solids is in the residual fraction, which is "inconsequential to barium bioavailability, mobility or reaction in the natural environment". Results from ESG (2003a) (see Appendix VI) showed soluble barium concentrations in pore water within soil-plant microcosms increased over 14 days after barite was added; however, final soluble barium concentrations remained low. The greatest increase was observed for 100% barite, where soluble barium increased from 0.3 to 2.4 mg/L over 14 days. Nelson *et al.* (1984) reported that the barium present as barite in drilling mud was not bioavailable to Swiss chard or ryegrass during a greenhouse study. However, trace elements co-precipitated into barite were available for plant uptake. Nelson *et al.* (1984) concluded that plants took up arsenic, cadmium, copper, lead, nickel, and zinc from drilling fluids.

Deverel *et al.* (1986) state that for sulphate to be reduced to sulphide in soil (and hence for soluble Ba^{2+} to be released from barite), highly reducing conditions are required. Sulphate reduction can occur in soil at a redox potential of approximately –240 mV (Lindsay, 1979 cited in Branch *et al.* 1990), which is considered "much reduced" (Branch *et al.* 1990). Branch *et al.* (1990) evaluated barium solubility in flooded and aerated non-hazardous oilfield waste and found that flooded oil field waste could develop very low redox potentials; however, the presence of high sulphate ions (either present in the oilfield waste originally or added as gypsum) prevented the increase of barite solubility under flooded and high soluble salt conditions. The authors suggest that increased barite solubility could occur under low sulphate conditions.

Deuel and Freeman (1989) demonstrated the conversion of barite to soluble barium in soil under anaerobic conditions in the laboratory. Deverel *et al.* (1986) also reported anaerobic reduction of sulphate to sulphide in three organic soils. In contrast, Deuel and Holliday (1990), Campbell Wells Corporation/K. W. Brown and Associates Inc. (1989; cited in US EPA, 1991), and Branch *et al.* (1990) found that anaerobic conditions did not result in increased barium ion concentrations in drilling mud waste. Deuel and Holliday (1990) conducted their experiment under anaerobic conditions normal for drill pit fluids in the absence of air. US EPA (1991) reviewed these studies and concluded that the anaerobic solubilization of barite can generate soluble forms of barium that may be transported to surface water and groundwater.

Freeman and Deuel (1984) reported that plants grown in barite-rich oilfield waste in wetlands contained more barium than plants grown in wetland background soil; however, the increase in barium content was not significant and barium concentrations in plants were below those shown to adversely affect plant yield (Freeman and Deuel, 1984). In addition, this study found that for one plant species (*Bacopa monnieri*) 65% of the variability in plant barium

content could be explained by soil pH; this plant species absorbed less soil barium at a lower pH.

The addition of barite at concentrations up to 300,000 mg/kg was found to increase soil pH and decrease soil moisture; however, conditions remained within the range supportive of plant and soil invertebrate survival and growth. Soil electrical conductivity was not affected by the addition of barite (ESG, 2003a). Miller (1980) reported a slight increase in pH (from 6.0 to 6.7) and a substantial increase in electrical conductivity (0.34 to 1.01 mmhos/cm) upon the addition of bentonite and barite to soil.

Fedorak and Gamez (2003) (see Appendix IV) investigated the effect of different redox conditions on barite solubilization with a matrix of Alberta clay-till soils. The range of reducing conditions that they considered included aerobic, nitrate-reducing, manganese-reducing, iron-reducing, sulphate-reducing, and methanogenic conditions. Their microcosms included soils contaminated with barite and hydrocarbon (from diesel-based muds disposed of in an old oilfield sump), and background soils either spiked or not spiked with barite. Some microcosms were supplemented with an electron donor (glucose or lactate) while others were not supplemented. The results of this work indicate that:

- Ba^{2+} could be released at low concentrations (typically 3 – 6 mg Ba^{2+}/kg soil, but no more than 14 mg Ba^{2+}/kg soil) from either soil or barite when a supplementary electron acceptor (glucose or lactate) was provided in excess.
- However, in absence of supplementary excess glucose or lactate (as would be the case in the environment), either no Ba^{2+} was released, or no more Ba^{2+} was released from soils spiked with barite than from unspiked soils.

A study commissioned for this project investigated the possible mobilization of barium by salts, and is reported in Appendix V. The purpose of this study was to determine whether a release of oilfield brine could result in the mobilization of barium from barite. The study concluded that the addition of sodium chloride could result in the release of barium from soil; however, sodium chloride did not cause the release of barium from barite.

4. BEHAVIOR AND EFFECTS IN BIOTA

The following section discusses the behaviour and effects of barite in terrestrial biota.

4.1 Soil Microbial Processes

No information was found concerning the effects of barite on soil microorganisms or soil microbial processes. Barite has a very low aqueous solubility and its biological uptake by soil microorganisms is expected to be limited under most natural soil conditions. Under non-saturated conditions and within the typical range of environmental pH values, barite solubility in soil is unlikely to increase (Deeley and Canter, 1986).

Dissolved barium may, however, be released from barite under sulphate-reducing conditions and could then have a negative effect on some soil microorganisms. Intracellular barium concentrations of 0.58 µg/mg (dry weight) were sufficient to inhibit microbial growth in sulphur-reducing bacteria (Baldi *et al.*, 1996). However, information in the scientific literature on the effects of barium to soil microorganisms is limited (CCME, 1999 and updates).

4.2 Terrestrial Plants

Although barite may be deposited onto leaves or be present in soil, barite is not considered bioavailable to plants due to its low aqueous solubility (CCME, 1999 and updates). Nelson *et al.* (1984) concluded that barium from barite was not available to Swiss chard and ryegrass grown in soil containing drilling fluids and that the concentration of barium in soil/drilling fluid mixtures was not predictive of total of barium concentrations in plant tissues. Freeman and Deuel (1984) found that plant uptake of barium in wetlands was not dependent on the concentration of measured plant-available barium in the soil/drilling fluid due to temporal variability in available barium measurements.

Soluble forms of barium (released from barite) may become available to plants for uptake under reducing conditions (Freeman and Deuel, 1984; Deuel and Holliday, 1998). The metabolic fate, behaviour, and toxicity of barium in terrestrial plants are discussed by CCME (1999 and updates).

4.2.1 Metabolic Fate and Behaviour

Barium is not an essential plant nutrient (Vanselow, 1966 cited in Deuel, 2003). A discussion of the metabolic fate of barite was not possible due to a lack of available information.

4.2.2 Toxicity

Barite Toxicity

Selected toxicological studies on the effects of barite on plants are presented in Table 2.

Toxicity studies by ESG (2003a) (reproduced in Appendix VI) indicated that the toxicity of barite to three plant species is very low. Plant toxicity tests for barite were conducted using alsike clover (21-d), orchardgrass (*Dactylis glomerata*; 14 d), and perennial ryegrass (*Lolium perenne*; 14-d) grown in a clay till soil amended with barite to achieve concentrations ranging from 1,000 mg barite/kg dry weight soil to 100% barite (1,000,000 mg barite/kg dry weight soil). Seedling growth was generally unaffected by barite content and the reduced root length in alsike clover observed at 50,000 mg barite/kg dry weight soil during the range finding test was not confirmed in following tests. The only adverse effects observed were the following:

- alsike clover emergence was reduced in 100% barite, but not at lower concentrations;
- alsike clover shoot length was reduced in 100% barite, but not at lower concentrations; and,
- perennial ryegrass root length was reduced in 100% barite, but not at lower concentrations.

Emergence in alsike clover may have been reduced because barite is a very dense growing matrix and not due to a toxicity response (ESG, 2003a). Where possible, linear regression analysis was performed on data to calculate inhibition concentrations (IC). The only IC values that were lower than 100% barite were IC_{20} values of 850,000 and 960,000 mg/kg for root length in orchardgrass and perennial ryegrass, respectively (ESG, 2003a).

Miller *et al.* (1980) added barite to soil to assess potential impacts to the growth of green beans (*Phaseolus vulgaris* L., 'Tendergreen') and sweet corn (*Zea mays* var. saccharata (Sturtev.), 'Bailey' Northrup King-199). To simulate two ways in which barite could be introduced to the soil of an oilfield site, barite was 1) incorporated into soil at 227,500 mg barite/kg air dry soil to imitate barite disposal and disking into the soil and 2) added at a higher concentration (795,300 mg barite/kg air dry soil) to imitate an accidental barite release. Neither barite treatment significantly reduced the growth of above ground green bean plant parts. A barite concentration of 795,300 mg/kg reduced sweet corn growth by 20%, but a concentration of 227,500 mg/kg had no effect.

Toxicity of Soluble Barium Compounds

The toxicity of soluble barium compounds (chloride and nitrate salts) to plants (peas, green beans, barley) has been investigated by a number of authors. However, the results of these tests are not relevant to this project since barium is expected to be much more available from soluble compounds than from the sulphate.

Stantec (2003) conducted a study of the toxicity of barium acetate to plants, specifically for this project. The rationale for the study is discussed further in Section 6.2.3, the study itself is reproduced in Appendix VII and the data analyzed in Appendix VIII. Essentially, the Stantec

(2003) study correlates the toxic response from barium acetate to the concentration of extractable barium measured in the soil. Extractable barium is a measure of the barium in solution in the porewater together with the barium sorbed to clay surfaces, and is intended as an approximation of the barium available to plants and soil invertebrates. The methodology for analyzing extractable barium is discussed in Section 6.2.2.

4.3 Terrestrial Invertebrates

4.3.1 Metabolic Fate and Behaviour

No information on the metabolic fate and behaviour of barium (as barite) in soil invertebrates was found.

4.3.2 Toxicity

Barite Toxicity

Selected toxicological studies of barite effects on soil invertebrates are presented in Table 3.

Three studies on four species of terrestrial invertebrate found no adverse effect on survival at the maximum concentrations investigated. Simini *et al.* (2002) investigated the effect of barite on the earthworm *Eisenia fetida*, and found no effect at their highest concentration of 17,000 mg barite / kg soil (10,000 mg barium / kg soil). Kuperman *et al.* (2002) investigated the effect of barite on the Enchytraeid worm *Enchytraeus crypticus*, and found no effect at their highest concentration of 17,000 mg barite / kg soil.

Studies by ESG (2003a) found no effect on invertebrate survival at any concentration. A 14-d acute toxicity test for barite was performed on earthworms (*Eisenia andrei*) and springtails (*Onychiurus folsomi*) using a clay till soil amended with barite to achieve concentrations ranging from 1,000 mg barite/kg dry weight soil to 100% barite (1,000,000 mg barite/kg dry weight soil). No earthworm or springtail mortality was observed during the duration of the test.

Toxicity of Soluble Barium Compounds

The toxicity of soluble barium compounds (acetate and nitrate salts) to terrestrial invertebrates (enchytraeids, earthworms, collembola) has been investigated by a number of authors. However, the results of these tests are not relevant to this project since barium is expected to be much more available from soluble compounds than from the sulphate. Stantec (2003) conducted a study of the toxicity of barium acetate to terrestrial invertebrates, specifically for this project, which is reproduced in Appendix VII and analyzed in Appendix VIII.

4.4 Livestock and Wildlife

4.4.1 Metabolic Fate and Behaviour

No information on the metabolic fate and behaviour of barium (as barite) in livestock or wildlife was found. There is no known function of barium in animals (Vanselow, 1966 cited in Deuel, 2003)

4.4.2 Toxicity

No information on the toxicity of barium (as barite) in livestock or wildlife was found.

4.5 Bioaccumulation

No information was available on bioconcentration factors from barite into soil or plants. However, bioconcentration factors for barium in soil into a variety of plants (0.4) and bioaccumulation factors for terrestrial insects (0.2) were developed following a field study with one sampling event (Hope *et al.*, 1996 cited in WHO, 2001).

5. BEHAVIOUR AND EFFECTS IN HUMANS AND MAMMALIAN SPECIES

US EPA (1991) considered barite to be non-toxic as it exhibits no evidence of carcinogenicity, developmental toxicity, reproductive toxicity, neurotoxicity, gene mutation, or chronic toxicity related to exposure. However, the barium ion is toxic if in an available form. The toxicity of the barium ion depends on the solubility of the barium compound. The low toxicity of barite to humans and environmental receptors is largely due to its insolubility in water, weak acids, and alcohols (US EPA, 1991). There is no known function of barium in animals (Vanselow, 1966 cited in Deuel, 2003). Acute and Chronic toxicological studies of barite effects on mammalian species are presented in Tables 4 and 5, respectively.

5.1 Pharmacokinetics

5.1.1 Absorption

Inhalation

In the respiratory system, the solubilization of inhaled barite and subsequent absorption of barium has been demonstrated in a number of studies by clearance of barite from the respiratory system followed by the excretion of barium in urine (Morrow *et al.*, 1964; Cember

et al., 1961 cited in Cuddihy and Griffith, 1972) or the presence of barium in the lymph system (Takahashi and Patrick, 1987).

The time taken to clear barite from the respiratory system was found to be proportional to the solubility of barium compounds as inhaled $BaCl_2$ was cleared more readily from the pulmonary system than barite (Cuddihy *et al.*, 1974). Morrow *et al.*, (1964) also found that in the first 24 h after inhalation, the clearance of insoluble dusts from the lungs of beagles increased with dust particle size.

Barite may be cleared from the respiratory tract by mucociliary mechanisms, lung-to-blood transfer, or potentially, solubilization in the tracheal wall. In beagle dogs, approximately 75% of inhaled barite was deposited to the pulmonary region and 25% entered the tracheobronchial and nasopharyngeal regions (Cuddihy *et al.*, 1974). In rats, 15.3% of intratracheally-injected barite was cleared from the lungs within 24 h; 7.9% was cleared by mucociliary mechanisms (removed material is eventually swallowed) and 7.4% was cleared by lung-to-blood transfer. The half time for each process was 9 h during the first 24 h after administration (Spritzer and Watson, 1964). Barite inhaled at a concentration of 1.1 µg/L for 30 to 90 min had a biological half time of 8 days in the lower respiratory tract of beagles (Morrow *et al.*, 1964). Takahashi and Patrick (1987), intratracheally administered barite to the caudal trachea (injection site). After 7 days 0.41% of the original barium dose remained; 10 times this level of barium had moved to the cranial region of the trachea. After 7 days, barite was cleared exponentially from the caudal trachea with a half time of 88 days and from the cranial trachea with a half time of 66 days. Barium in the trachea of rats was detected up to 6 months after injection. Takahashi and Patrick (1987) concluded it was possible that some of the barite had been cleared from the tracheal wall by solubilization, but barium concentrations in blood, and the entire carcass (including skeleton) were found to be low. US EPA (1991) stated that in rats following intratracheal installation, approximately 1.3% of the barium in barite was absorbed via solubilization (US EPA, 1991).

In the body, barite particles are often engulfed by macrophages, which do not appear to suffer any toxic effects at a dose of 10 barite particles per macrophage cell (Rae, 1977). Macrophages have been reported to engulf barite particles in the lungs (Parkes, 1982 cited in BIBRA, 1994), tracheal wall (Stirling and Patrick, 1980, cited in Takahashi and Patrick, 1987), and gastrointestinal tract (Najjar *et al.*, 1973 cited in Shackleton *et al.*, 2000; Shackleton *et al.*, 2000). Takahashi and Patrick (1987) were not able to determine whether barite particles retained in the trachea by macrophages had become solubilized *in situ*.

Oral

Barite solubilization and subsequent barium absorption has been demonstrated from the gastrointestinal tract as evidenced by increased barium concentrations in blood and urine. A single, low dose of barite (0.5 mg/kg body weight) given to rats by gavage was absorbed at an

equivalent rate to a similar concentration of $BaCl_2$ (a much more soluble barium salt). McCauley and Washington (1983) attribute the absorption of barium at low barite concentrations to solubilization in the gastrointestinal tract by stomach acids.

When large doses of barite are administered orally, only a very small fraction of the barite is solubilized by gastric hydrochloric acid and absorbed (*e.g.*, prior to gastrointestinal x-ray). However, barium levels in the blood and urine of humans were found to increase significantly following ingestion of 58 to 400 g of barite in radio-opaque contrast materials (Mauras, *et al.*, 1983, Claval, *et al.*, 1987 cited in US EPA, 2005a). Barite solubilization, which led to the fatal barium poisoning of a patient who had an impaction of the colon following the oral administration of barite, may have occurred due to cationic exchange in the intestinal tract where barite was converted into barium chloride and absorbed by the intestinal mucosa (Pélissier-Alicot *et al.*, 1999). Elevated barium concentrations were observed in the blood and cerebrospinal fluid of this patient.

Dodd et al. (2007) report on a series of bioaccessibility studies for barite in soil. This report is included as Appendix II. Bioaccessibility studies attempt to simulate the conditions (pH, enzyme mix, temperature, agitation, residence time etc.) in the stomach and small intestine under *in vitro* conditions, and determine how much of the metal in question becomes solubilized and hence available for absorption. Metal that does not become solubilized is not available for absorption in the small intestine, and accordingly, *in vitro* bioaccessibility measurements are often taken as a conservative estimate of bioavailability. Dodd et al. (2007) interpreted the results of a wide range of bioaccessibility tests for barite-contaminated soils to indicate a bioaccessibility of 55% based on low concentrations of barite (30 to 300 µg of barite-barium in 100 mL of solution. These authors noted that a lower proportion of barium was extracted at lower fluid:soil ratios.

Dermal

No information on the dermal absorption of barite was available found, but dermal absorption of barite is not expected (US EPA, 1991).

5.1.2 Distribution

Inhalation

In the body, the greatest concentrations of barium are found in the skeletal system (US EPA, 2005a) and absorbed barium from inhaled barite has been measured in the skeletal system. Cuddihy *et al.* (1974) reported approximately 25% of absorbed barium (from inhaled barite) was transported to the skeleton. In contrast, Takahashi and Patrick (1987) found that only 0.84% of the barium (as barite) injected into the tracheas of rats, was present in the carcass (including the skeleton) after 7 days, 1.3% was present after 4 weeks, and 1.1% was present

after 24 weeks. Differences in the results of these two studies may have been due to the preparation and resulting solubility of barite particles (Takahashi and Patrick, 1987). Within 10 days of an intratracheally-injected dose of barite, rats excreted approximately 5% of the initial dose in urine (Cember *et al.*, 1961 cited in Cuddihy and Griffith, 1972).

Takahashi and Patrick (1987) demonstrated that barite administered to the tracheal lumen drained to the lymph nodes in the thoracic cavity and the deep and superficial cervical regions, but the proportion of barium cleared from the trachea through these routes was impossible to quantify. Alveolar macrophages can also remove barite from alveoli in the lungs to regional lymph nodes (Buschman, 1991).

Oral

McCauley and Washington (1983) compared the absorption and distribution of barium from barite and $BaCl_2$ (administered orally at low doses) to rats over a 2-hour period. Similarities in barium absorption and distribution to the eye 2 hours after exposure led them to conclude that the distribution of barium from both compounds to heart, liver, kidney, and skeletal muscle was similar. Measured concentrations of absorbed barium in the heart, eye, skeletal muscle, and kidneys were greater than the whole blood concentration, which suggests barium may concentrate in soft tissue.

5.1.3 Metabolism

No information on the metabolism of barite was found.

5.1.4 Elimination

Absorbed barium from inhaled barite is primarily excreted from the body in feces and urine. Cuddihy *et al.* (1974) found approximately 75% of absorbed barium (from inhaled barite) was excreted in the urine and feces over a 2 wk period by beagles. Approximately 6% of the initial lung deposit of intratracheally-injected barite was excreted in the urine of rats (Spritzer and Watson, 1964). Cember *et al.* (1961 cited in Cuddihy and Griffith, 1972) found that within 10 days of an intratracheally injected dose of barite, rats excreted approximately 5% of the initial dose in urine. Morrow *et al.* (1964) reported that barium (from inhaled barite) was so rapidly excreted in the feces and urine of beagles within one week of exposure, the study of barite elimination over a long period of time was not possible.

Some barium taken up by organisms may accumulate in their body tissues. Bioaccumulation factors for white-footed mice (0.02) and hispid cotton rats (0.02) were developed following a field study with one sampling event. Barium was lost from these receptors at a fairly rapid

rate and depuration rates of 0.4/day and 0.2/day were estimated for white-footed mice and hispid cotton rats, respectively (Hope *et al.*, 1996 cited in WHO, 2001).

5.1.5 Modifying Factors

No modifying factors for barite pharmakokinetics were found.

5.2 Mammalian Toxicology

Acute and chronic toxicological studies of barite effects on mammalian species are presented in Tables 4 and 5, respectively.

5.2.1 Acute Toxicology

Inhalation

A single intratracheal dose of 0.6 ml/kg Ba147 (a preparation containing 85% barite) to rabbits did not cause treatment-related effects to pulmonary ventilation, blood gas levels, or lung weights up to 4 weeks after administration. Dose related shadows were observed in lungs and 78% of animals exhibited bronchopneumonia, bronchitis, or bronchiolitis one week after dosing. Further details on this study were not available as US EPA was only able to obtain an English abstract (Uchiyama, *et al.*, 1995 (abstract) cited in US EPA, 2005a). Stirling and Patrick (1980, cited in Takahashi and Patrick, 1987) reported that 1 to 7 days after barite was injected into the trachea of rats, barite particles retained in the tracheal wall were located within macrophages.

Oral/Gastrointestinal Tract

Boyd and Abel (1966) administered barite to rats through an intragastric cannula. No deaths were caused by dosages up to 160 g barite/kg body weight in a pilot test. Definitive tests found a single intragastric administration of barite to rats at doses of 25 to 40% body weight caused death by stomach rupture or bowel obstruction, intestinal bleeding and generalized blood clotting. The LD_{50} for stomach rupture was 307 +/- 29 g barite/kg body weight and for bowel obstruction was 364 +/- 41 g barite/kg body weight (Boyd and Abel, 1966).

5.2.2 Sensitization and Irritancy

Barite may cause brief inflammatory responses or ulcers in wounds. The intestinal tissue of 20 dogs exhibited an inflammatory response (especially by neutrophilic granulocytes) when exposed to barite. Once the barite had been engulfed by macrophages, the inflammatory response rapidly decreased (Najjar *et al.*, 1973 cited in Shackleton *et al.*, 2000). In dogs, ulceration was observed when a deep colorectal biopsy was immediately followed by a

barium enema; however, the healing process was comparable to wounds with no barite added (Maglinte *et al.*, 1983 cited in Shackleton *et al.*, 2000). Shackleton *et al.* (2000) reported no effect of barite application on wound healing, granuloma formation, weight gain, activity, and survival of rats with gastrointestinal wounds (stomach, small bowel and colon).

5.2.3 Short-Term Toxicity/Subchronic Toxicity

No information on the subchronic toxicity of barite was found.

5.2.4 Immunotoxicity

No information on the immunotoxicity of barite was found.

5.2.5 Long-Term/Chronic Toxicity

Inhalation

Holusa *et al.* (1973, cited in BIBRA, 1994) exposed rats to atmospheres containing 40 mg/m^3 barite for 5 h/day for up to two months. Following barite exposure, the lungs and associated lymph nodes were examined at a microscopic level. Holusa *et al.* (1973, cited in BIBRA, 1994) described inhaled barite as an "inert dust" based on the pattern of tissue changes observed in the lungs.

Oral

To determine whether heavy metals (including barium) could be safely used as nutrient markers, Hutcheson *et al.* (1975) fed barite, scandium, chromium, lanthanum, samarium, europium, dysprosium, terbium, thulium, and ytterbium oxides to three generations of mice. The barite concentration of this mixture ranged up to 8 ppm (approximately 1.2 mg/kg bw/day). The body weight gain, mortality rate, reproduction, lactation, and general appearance of mice in the 8 ppm barite treatment, and the gross appearance of organs and blood chemistry of mice in the 0.8 ppm barite treatment were not overtly affected by barite consumption at these levels.

5.2.6 Carcinogenicity

Studies on the potential carcinogenicity of barite were not available for any route of exposure; however, NTP (1994) found no evidence of carcinogenic activity of barium chloride dihydrate in rats or mice exposed for 2 years via drinking water. Barium chloride dihydrate is more soluble than barite and so the barium bound in barium chloride dihydrate is expected to be more bioavailable to organisms. Extrapolation of the NTP (1994) study results to barite

lead to the conclusion that barite is not likely a carcinogen in mammals. A toxicity review by US EPA (1991) found no evidence for cancer associated with barite exposure.

A local cancer (mesothelioma) developed in 1 of 30 treated rats which had barite injected directly into the pleural cavity (Wagner *et al.*, 1973 cited in BIBRA, 1994).

5.2.7 Mutagenicity

The Registry of Toxic Effects of Chemical Substances (NIOSH, 1994 cited in BIBRA, 1994) describes barite as a mutagen because chromosome damage was reported for mice that received an intraperitoneal injection of 12.5 mg barite/kg bw. However, "the study report in question is in Chinese (Laifu *et al.*, 1986), but the English abstract refers to the testing of a beryllium compound and not barium sulphate" (BIBRA, 1994).

5.2.8 Neurotoxicity

No information on the neurotoxicity of barite was found.

5.2.9 Reproduction

Three generations of mice fed barite at concentrations up to 8 ppm (approximately 1.2 mg/kg bw/day) along with a number of lanthanide metal oxides, showed no effects on the number of females having litters, average litter size, or average weaning weight (Hutchenson *et al.*, 1975).

5.2.10 Teratology

No information on the teratology of barite to mammalian species was found during the preparation of this report.

5.3 Human Toxicology

5.3.1 Acute Toxicology

Inhalation

The aspiration of small amounts of barite into lungs is almost always inconsequential (Ott and Gelfand, 1983) and has led to its use as a bronchiographic contrast agent. Buschman (1991) reported that barite suspensions, administered during bronchography, were retained for years in the lungs through alveolarization and the likely incorporation of barium into macrophages. Retained barite was present in the peripheral airways and alveoli, beyond the ciliated mucosa,

and could not be effectively cleared from the lungs. This residual barite did not cause any fibrotic pulmonary changes or toxicity problems after 6 months of retention, but interfered with subsequent imaging procedures (Bushchman, 1991).

Injection

During administration of barite as a contrast agent, perforation of the esophagus, stomach or duodenum may allow the extravasation of barite to into the mediastinum or peritoneal cavity, and result in mediastinitis with an accompanying bacterial infection and peritonitis, respectively (Ott and Gelfand, 1983). Enema complication may also inject barite into the bloodstream where extensive blood clotting in the lungs and heart could potentially be fatal (Ansell, 1976; Blom *et al.*, 1983; Juler *et al.*, 1975; Seaman and Wells, 1965 cited in BIBRA, 1994) or into the vagina causing venous intravasation or vaginal rupture with extravasation (Ott and Gelfand, 1983).

Oral

Boyd and Abel (1966) extrapolated the results of their experiments on albino rats and concluded that humans could not orally ingest enough barite in a single dose to be acutely toxic. However, impaction of the colon has been reported in some case studies following the oral ingestion of large doses of barite prior to gastrointestinal x-ray (US EPA, 1991) and may be fatal (Pélissier-Alicot *et al.*, 1999). Pélissier-Alicot *et al.* (1999) describe a case study where an unknown intestinal occlusion caused impaction of the colon and led to the intravasation or venous embolization of barite, which had been ingested prior to gastrointestinal x-rays.

5.3.2 Sensitization and Irritancy

The impaction of barite particles into the skin, resulting from the explosion of golf balls, may cause the formation of granulomas (a mass or nodule of chronically inflamed tissue produced in response to foreign particles) (Honda and Nishi, 1978 and Ishii *et al.*, 1982 cited in BIBRA, 1994). Imperfectly administered enemas have also been reported to cause rectal granulomas, barium inflammation of the abdomen, and embolization (*e.g.*, Beddoe *et al.*, 1954; Carney and Stephens, 1973; Weitzner and Law, 1972 cited in BIBRA, 1994).

Low incidences of severe adverse reactions have been reported by a number of researchers following the administration of barite meals or enemas. These severe reactions are listed by BIBRA (1994) and include respiratory difficulties, generalized skin rash, abrupt decreases in blood pressure, and fatalities. Most researchers concluded these hypersensitivity reactions were not caused by barite, but by other components in the barite suspension although this hypothesis was rarely confirmed (BIBRA, 1994)

5.3.3 Short-Term/Subchronic Toxicity

Repeated use of barite as a contrast agent prior to gastrointestinal x-rays has little physiological effect other than volume and fluidity changes (Ott and Gelfand, 1983).

5.3.4 Immunotoxicity

No information on the immunotoxicity of barite to humans was found during the preparation of this report.

5.3.5 Long-Term/Chronic Toxicity and Carcinogenicity

Inhalation

Chronic inhalation of barite dust causes baritosis (a benign pulmonary reaction) characterized from x-rays by dense, discrete, small opacities. These opacities are barite particles not tissue lesions (US EPA, 1991). Macrophages engulf the particles and negligible effects to the lung tissue occur (Parkes, 1982 cited in BIBRA, 1994). Baritosis does not have any symptoms and does not decrease pulmonary function (US EPA, 1991). Once exposure has ended, opacities slowly reduce (Doig, 1976).

No studies that addressed the potential carcinogenicity of barite to humans were found during compilation of this report. Barium is classified as Group D – not classifiable to human carcinogenicity by US EPA (2005a) because animal studies have not adequately addressed barium carcinogenicity through the inhalation route of exposure.

5.3.6 Neurotoxicity

Neurological and cardiovascular effects were observed following the barium poisoning of a patient who had been orally administered barite prior to gastrointestinal x-rays. An intestinal occlusion of unknown origin caused the barite to remain in the digestive tract. Convulsive seizures and encephalopathy were observed prior to death; these symptoms have been described by previous reports of barium poisoning (Pélissier-Alicot *et al.*, 1999).

5.3.7 Reproduction

No information on potential human reproduction effects from barite exposure was found during the preparation of this report.

5.3.8 Teratology

No information on the teratology of barite to humans was found during the preparation of this report.

5.3.9 Epidemiology

No information on the epidemiology of barite exposure for humans was found during the preparation of this report.

5.4 Human Tolerable Daily Intake

Much of the available data suggest that barite is likely to be significantly less toxic to humans than soluble forms of barite. However, none of the available studies were suitable for developing a human tolerable daily intake (TDI) for barite. In the absence of such studies, the conservative assumption is made that the TDI for barite is the same as for soluble forms of barium.

The toxicology of barium has been reviewed by Health Canada and the US EPA. Health Canada developed a Canadian Drinking Water Quality Guideline (CDWQG) of 1.0 mg/L (Health Canada 1990), based on an epidemiological study of barium in drinking water by Brenniman and Levy (1984). Health Canada (2004) calculated a TDI of 0.016 mg/kg-bw/day based on the CDWQG developed in Health Canada (1990).

More recently, the US EPA (2005a) reviewed the toxicology of barium and revised their previous (US EPA, 1999) reference dose (RfD, equivalent to a TDI) to give a new value of 0.2 mg/kg-bw/day. The previous US EPA (1999) RfD was based on a weight-of-evidence approach that focused on four coprincipal studies: the Wones *et al.* (1990) experimental study in humans, the Brenniman and Levy (1984) epidemiological study, and the NTP (1994) subchronic and chronic rat studies. The McCauley *et al.* (1985) study of unilaterally nephrectomized rats was used to support the identification of the kidney as a cocritical target. The US EPA (2005a) concluded that three out of the four studies previously considered (including the Brenniman and Levy (1984) study used by Health Canada, 1990) as coprinciple did not show convincing dose-response relationships, and accordingly, re-derived the reference dose based on the NTP (1994) 2 year barium chloride drinking water study in mice, with chemical-related nephropathy identified as the critical effect.

The point of departure used by the US EPA in deriving the reference dose was 63 mg/kg-bw/day which was the lower 95% confidence limit on the 5% modelled benchmark dose ($BMDL_{05}$) for male mice, corresponding to the dose that would be expected to cause no more than a 5% increase in chemical-related nephropathy in either sex of mouse. An uncertainty

factor of 300 was applied to this departure point, which was rationalized as a factor of 10 for extrapolating from mice to humans, a factor of 10 to account for variability in human sensitivity, and a factor of 3 for deficiencies in the database. This resulted in a calculated barium reference dose of 0.21 mg/kg-bw/day, which was rounded to 0.2 mg/kg-bw/day.

In considering the relative merits of the US EPA (2005a) RfD and the Health Canada TDI based on their 1990 toxicological review, the following points were considered.

- The US EPA (2005a) conducted a careful review of all the available literature.
- The US EPA (2005a) based their reference dose on a study (NTP, 1994) that was not available at the time of the Health Canada (1990) derivation.
- The US EPA (2005a) determined that the NTP (1994) study was a better basis for developing a reference dose than the Brenniman and Levy (1984) study used by Health Canada (1990).

Based on the above considerations, it was decided that the more recent US EPA (2005a) reference dose of 0.2 mg/kg-bw/day was more relevant than the older Health Canada TDI, and hence the US EPA (2005a) reference dose of 0.2 mg/kg-bw/day was used in this project to assess safe levels for human exposure.

5.5 Human Bioavailability

The information on oral absorption presented in Section 5.1.1 is conflicting. It is clear that barium can be solubilized from barite in the gastrointestinal tract and absorbed. At high barite doses (approximately 500-3,000 mg/kg-bw), only a small fraction of the barite is absorbed. Based on the work of McCauley and Washington (1983), at lower doses (0.5 mg/kg-bw) it appears that barite is absorbed at an equivalent rate to soluble forms of barium, implying a relative bioavailability of 100%. The bioaccessibility work by Dodd et al. (2007) includes barite concentrations equivalent to doses even lower than those used by McCauley and Washington (1983), and the authors suggest a bioaccessibility of 55% for barite-barium. Estimates of bioavailability of soluble barium compounds range from 0.7 to 85% (US EPA, 2005). Data is not available to estimate the bioaccessibility of soluble forms of barium used to derive the US EPA (2005) reference dose. Considering the conflicting nature of the available information, and applying the precautionary principle, it is considered that there is insufficient evidence at this time to support a barite-barium bioavailability of less than 100% relative to soluble barium for the purposes of guideline development, and accordingly, this is the value used in this document.

5.6 Human Exposure

Insufficient information was available to assess the typical exposure of the Canadian population to barite. However, Health Canada (1990) has assessed the exposure of the Canadian population to barium. According to Health Canada (1990) intake of barium through inhalation would be negligible compared with the amount ingested and the primary exposure to barium is through food, with drinking water being significant in areas where barium levels in drinking water are high (0.6 mg/L). Health Canada (1990) estimated the mean daily intake of barium to be slightly more than 1 mg/day, which corresponds to an estimated daily intake of 0.014 mg/kg-bw/day for a 70.7 kg adult.

6. SPECIAL CONSIDERATIONS IN THE DEVELOPMENT OF BARITE GUIDELINES

6.1 Introduction

Typically guidelines for metals are developed for a single element (*e.g.*, barium), rather than a compound such as barite. Developing guidelines for inorganic compounds presents particular challenges, some of which are discussed below.

Barite is highly insoluble, and as such is expected to be largely unavailable. Accordingly, barite can be managed safely in the environment at higher concentrations than would be appropriate for soluble barium compounds. However, while barium analysis is routinely carried out on environmental soil samples, there is no commercial analytical method presently available to analyze specifically for barite.

A typical situation at upstream oil and gas sites (and potentially other sites where barite has been used) is that barium is present at levels above generic guidelines, but, based on the site history, the source of the barium is assumed to be barite. Before barite guidelines can be applied at such a site, it will be necessary to demonstrate:

i. that the barium is still in an immobile/unavailable form; and,
ii. that the barium would not be expected to become more mobile/available in the future.

Studies were commissioned as part of the current project to help resolve these two issues. The studies and their application are discussed in Sections 6.2 and 6.3.

6.2 Barium Speciation

As noted above, there is no commercially available method for determining the speciation of barium in a soil sample. However, the question of whether the available barium in a soil sample is above or below the level that might cause adverse effects to plants or soil invertebrates can be addressed by correlating the toxic response in plants and invertebrates with the level of available barium. The selection of an analytical method for available barium is discussed in Section 6.2.1. The recommended method for analysis of extractable barium is provided in Section 6.2.2. A toxicity testing program using barium acetate is discussed in Section 6.2.3.

6.2.1 Available Barium

Three techniques for barium analysis were investigated to determine which of them would provide good correlations between the amount of barium measured and the toxic responses of the plants or invertebrates to barium acetate (see following Section). The three techniques were:

1. conventional soil analysis for barium involving an acid digest, followed by inductively coupled plasma – optical emission spectrometry (ICP-OES) detection;
2. ICP-OES analysis of a saturated paste extract; and,
3. ICP-OES analysis of the extractable barium (see Section 6.2.2).

Conducting these analyses on samples from the toxicological work reported in Appendices VI and VII indicated that neither technique 1 nor technique 2 was a good predictor of toxic response in plants or invertebrates. Technique 1 appeared to respond to barium that was not available to the biota, presumably because barium was released from mineral grains during the acid digest. Technique 2 did not respond to barium that was causing a toxic response in plants, possibly because barium sorbed to clay surfaces is available to plants but is not measured by the technique.

Initial tests of technique 3, however, indicated a much better correlation between analytical results and toxicological response. Accordingly, it was determined that extractable barium was likely to be the best measurement of available barium. John Ashworth and Warren Greig of EnviroTest Laboratories in Edmonton and Saskatoon, respectively, developed an analytical methodology for extractable barium. Method development was conducted in two phases. The first phase involved a number of trials to select the most effective extraction methodology. The technique presented in the following Section (6.2.2) was developed to maximize recovery of sorbed barium, and to minimize ICP-OES interference from high concentrations of cations in the extractant. The second phase of method development involved ruggedness testing on the proposed analytical method to determine to what extent

the method might be sensitive to small changes in technique. The results of ruggedness testing are included in Appendix III, and indicate that the methodology presented below is suitably rugged.

6.2.2 Analytical Method for Extractable Barium

The recommended procedure for determination of extractable barium (see also Appendix III) is as follows:

- Prepare 0.1 M calcium chloride (14.7 g of pure dihydrate per litre of de-ionized water).
- Use a representative sub-sample of air-dried, <2 mm soil, weighing at least 10 g.
- Add 0.1 M calcium chloride at a 1:10 ratio, *e.g.*, 10 g soil plus 100 mL, leaving adequate headspace for agitation.
- Agitate for at least 2 h on either a platform or end-over-end shaker.
- Filter the extract either by gravity or under suction, using a filter paper fine enough to yield a clear filtrate.
- Make up standard solutions (*e.g.* of barium acetate or chloride) either in DI water or in the extracting solution.
- Analyze the filtrate and standards by ICP within 24 h.

6.2.3 Barium Acetate Toxicity Testing

A program of acute and definitive toxicity testing using barium acetate with three species of plants and two species of invertebrates was commissioned for this report (Stantec, 2003; reproduced in Appendix VII). The purpose of this testing was to correlate the toxic response observed in plants and soil invertebrates with the concentration of extractable (*i.e.*, available) barium. It should be noted, however, that the results in Stantec (2003) are all presented in terms of nominal concentrations (*i.e.*, the mass of barium acetate added), rather than the mass of barium in the sample.

An analysis of selected samples from the toxicity testing program for extractable barium is presented in Appendix VIII. The regression of extractable barium was analysed against the mass of barium acetate added, and the toxicity testing results were expressed in terms of measured concentrations of extractable barium.

6.3 Barium Mobilization

Two studies were commissioned through the Microbiology Department of the University of Alberta, supervised by Dr. Phil Fedorak, to help determine whether the possibility of future mobilization of barium from barite was a significant concern.

6.3.1 Soil Microcosm Study

This study (Fedorak and Gamez, 2003, included in Appendix IV and discussed in Section 3.3) investigated the possible mobilization of barium from barite as a result of microbial degradation, particularly the action of sulphate-reducing bacteria (SRB) on barite. Previous studies had shown that SRBs could mobilize barium from barite under favourable conditions, but none of the studies had used conditions that were particularly relevant to typical upstream oil and gas sites in Canada.

Fedorak and Gamez (2003) showed that while SRBs were capable of mobilizing barium from barite when a supplementary electron acceptor (glucose or lactate) was added, no barium was mobilized from barite in the absence of added glucose or lactate. In particular, the SRBs in these experiments did not seem able to utilize the contaminant hydrocarbon (weathered diesel fuel) in the soil as an electron acceptor. Even in the experiments where glucose or lactate was added, the amount of barium released from barite was relatively small (in all cases less than 12 mg barium released from barite per kg of soil, even though samples were spiked with 2,000 or 10,000 mg of barite per kg of soil).

Overall, it is not anticipated that barium mobilization due to bacterial activity will be a concern at typical upstream oil and gas sites.

6.3.2 Salt Mobilization Study

This study (included in Appendix V and discussed in Section 3.3) investigated whether salt (such as that associated with a release of oilfield brine) could result in the mobilization of barium from barite. The study found that while salt could release (naturally occurring) barium from soils, no barium was released from barite. Accordingly, barium mobilization from barite due to interactions with salt will not be a concern.

7. DERIVATION OF ENVIRONMENTAL SOIL REMEDIATION GUIDELINES

Environmental soil remediation guidelines were developed for five standard land uses: natural areas, agricultural, residential/parkland, commercial and industrial (AENV, 2009).

7.1 Soil Remediation Guidelines for Soil Contact

Two soil remediation guidelines for ecological soil contact were developed. The first is based on the concentration of extractable barium and is used as a screening tool to determine

whether the barite guideline can be applied. The second is the guideline for barite, and is based on the total barium concentration. Guideline application is discussed in Section 9.

7.1.1 Extractable Barium

The development of the soil contact guideline for extractable barium is described in detail in Appendix VIII, and summarized here.

Soil sample concentration series from either the beginning or end of five different toxicity tests from the Stantec (2003) program were analyzed for extractable barium. Since all five barium acetate/extractable barium curves essentially formed part of the same data set, it appeared that the measured concentration of extractable barium was independent of the species that was present in the toxicity test, and whether the sample was collected at the beginning or the end of the test. Accordingly, all five data sets were combined before generating a regression equation. A linear regression was fit to the data (Appendix VIII).

All the toxicity data in Stantec (2003) Appendix VII) were presented on a nominal barium acetate basis. In the present document, the 20th percentile effect data (*i.e.*, IC_{20}, EC_{20}, and LC_{20}) were used to compute the soil contact guidelines. The nominal 20th percentile data from Stantec (2003) were converted to an extractable barium basis by applying the regression equation to the nominal toxicity data. The different growth endpoints for each plant species were considered redundant, as were the different reproduction endpoints for springtails. Each group of redundant endpoints was combined as their geometric mean. The soil contact guideline for natural areas, agricultural land, and residential/parkland land uses was calculated as the 25th percentile of the geometric means, and was 250 mg/kg (rounded to 1.5 significant figures; Table 6). The soil contact guideline for commercial and industrial land uses was calculated as the 50th percentile of the geometric means and was 450 mg/kg (rounded to 1.5 significant figures; Table 6).

7.1.2 Total Barium Guideline for Barite Sites

If extractable barium concentrations at the site comply with the applicable extractable barium criterion, then the total barium at the site may be assessed against the total barium guideline for Barite Sites.

The soil remediation guideline for total barium at Barite Sites (see Section 9 for definition) is based on the barite plant and soil invertebrate studies discussed in Sections 4.2 and 4.3. Most studies found minimal effects on either plants or soil invertebrates. The soil remediation guideline for total barium at Barite Sites is conservatively set at the no observed adverse effect level (NOAEL) from the ESG (2003a) definitive plant tests on alsike clover and

perennial ryegrass. Both these tests had a NOAEL of 300,000 mg barite per kg soil, which corresponds to 180,000 mg barium per kg soil (Table 6).

7.2 Soil Remediation Guidelines for Soil and Food Ingestion

Insufficient data were available to calculate the food ingestion part of this guideline. However, it is not anticipated that bioconcentration of barite into plants will be significant. Nelson *et al.* (1984) reported that the barium present as barite in drilling mud was not bioavailable to Swiss chard or ryegrass during a greenhouse study. Freeman and Deuel (1984) reported that plants grown in barite-rich oilfield waste in wetlands contained more barium than plants grown in wetland background soil; however, the increase in barium content was not significant.

Accordingly, and consistent with the approach taken for similar cases in AENV (2009), a guideline (SQG_{ESI}) was calculated for ecological soil (but not food) ingestion for natural area and agricultural land use. A meadow vole was selected as the most exposed organism for both land uses, based on soil ingestion rate and body weight. The following equation was used:

$$SQG_{SI\text{-}L/W} = \frac{0.75 \times DTED \times BW \times 1{,}000}{SIR \times BF}$$

Where:

- $SQG_{SI\text{-}L/W}$ = ecological remediation guideline for soil ingestion livestock/wildlife (mg/kg);
- 0.75 = factor to prevent animals from being exposed to more than 75% of the DTED (unitless; AENV, 2009);
- DTED = daily threshold effect dose for mammalian species (51.8 mg/kg-bw/day; see Section 7.2.1 below);
- BW = body weight (meadow vole: 0.017 kg; cow: 550 kg);
- 1,000 = conversion factor from kg to g;
- SIR = soil ingestion rate (meadow vole: 0.058 g/day; cow: 747 g/day); and,
- BF = bioavailability factor (1; assumed).

Substituting these values in the above equation and rounding to 1.5 significant figures yields a value of 10,000 mg/kg for wildlife soil ingestion and 30,000 mg/kg for livestock soil ingestion (Table 6).

7.2.1 Daily Threshold Effect Dose

The CCME (2006) protocol for developing soil quality guidelines includes a procedure for developing a daily threshold effect dose (DTED) for grazing ungulates. Based on the requirements of the CCME (2006) protocol, insufficient toxicological data were available, and accordingly a DTED could not be calculated for barium by this method. However, it is noted that the CCME (2006) protocol for calculating DTEDs is not intended to apply to receptors other than grazing ungulates, and the limiting receptor being evaluated in this project is a meadow vole.

The US EPA (2005b) developed a wildlife toxicity reference value (TRV, equivalent to a DTED) for barium as part of their efforts to develop an Ecological Soil Screening Level (Eco-SSL). They conducted an extensive literature review which identified 837 papers with possible toxicity data for barium for either mammalian or avian species. Of these papers, 826 were rejected for various reasons, and of the remaining papers, 10 contained data for mammalian species. These papers were reviewed and data extracted and scored according to the standard procedures established for Ecological Soil Screening Level (Eco-SSL) derivation.

The US EPA (2005b) identified a total of 27 results, all for laboratory rodents, for relevant endpoints which had a data evaluation score of >65 and were considered in the derivation of the TRV. A geometric mean of the NOAEL values for growth and reproduction effects was calculated to be 51.8 mg/kg-bw/day. This value was lower than the lowest bounded LOAEL for reproduction, growth, or survival, and accordingly was adopted by US EPA (2005b) as the TRV.

Given that sufficient data were not available to meet the CCME (2006) protocol requirements, and also that all the 27 data points used to develop the US EPA (2005b) TRV were based on rodents of the family Muridae, the same family as the receptor being evaluated for this pathway (meadow vole), it was decided to adopt the US EPA (2005b) barium mammalian wildlife TRV of 51.8 mg/kg-bw/day as the DTED in this project.

7.2.2 Soil Ingestion Rate

The soil ingestion rate was calculated using the following equations:

$$SIR = FIR \cdot PSID$$

and

$$FIR = 0.0687 \cdot BW^{0.822} \cdot 1{,}000$$

Where: SIR = soil ingestion rate (meadow vole: 0.058 g/day, calculated below);
FIR = food ingestion rate (meadow vole: 2.41 g dry weight/day; calculated below);
PSID = percent soil in diet for meadow vole (2.4% – US EPA, 1993);
BW = body weight (meadow vole: 0.017 kg); and,
1,000 = conversion factor from kg to g.

Substituting these values in the above equation yields value for FIR of 2.41 g dry weight/day and for SIR of 0.058 g day.

7.3 Nutrient and Energy Cycling Check

This guideline was not calculated due to a lack of adequate data.

7.4 Off-Site Migration Check

The off-site migration check for ecological endpoints is calculated to ensure that wind and water erosion of contaminated material from a commercial or industrial site could not cause unacceptable contaminant concentrations on an adjacent property with a more sensitive land use. The check is calculated using the equation provided in AENV (2009):

$$SQG_{OM} = (14.3 \times SQG_A) - (13.3 \times BSC)$$

Where SQG_{OM}= soil remediation guideline protective of offsite migration (mg/kg);
SQG_A = soil remediation guideline for ecological receptors for agricultural land use (10,000 mg/kg, Table 6); and,
BSC = background soil concentration (325 mg/kg, Section 2.4.3).

Substituting these values in the above equation, and rounding to 1.5 significant figures, yields a value of 140,000 mg/kg, which is the ecological off-site migration check (Table 6).

7.5 Groundwater Check (Aquatic Life)

This check was not calculated because it is not applicable to metals (CCME, 1999 and updates).

7.6 Data Gaps

The available data were sufficient to develop soil contact guidelines both for total barium and for extractable barium.

Data on the effects of barite on soil microbial communities would be required to calculate the nutrient cycling check. However, based on the chemical inertness of barite, it is not anticipated that significant adverse effects would be found.

Further data on the bioaccumulation of barium from barite into plants would be required to calculate the food ingestion part of the livestock/wildlife soil and food ingestion guideline. However, based on the assumed low bioavailability of barite it is not anticipated that bioconcentration of barite from soil into plants would be significant.

8. DERIVATION OF HUMAN HEALTH SOIL REMEDIATION GUIDELINES

Human health soil remediation guidelines were developed for four standard land uses: agricultural, residential/parkland, commercial and industrial (AENV, 2009).

8.1 Soil Ingestion Guideline

The guideline for this exposure pathway was calculated based on the standard (AENV, 2009) equation provided below:

$$PSQG_{HH} = \frac{(TDI - EDI) \times SAF \times BW}{\left[(AF_G \times SIR) + (AF_L \times IR_S \times ET_2) + (AF_S \times SR)\right] \times ET_1} + [BSC]$$

Where:

SQC_{SI} = human health soil ingestion guideline (mg/kg);

TDI = tolerable daily intake for barium (0.2 mg/kg-bw/day; see Section 5.4);

EDI = estimated daily intake (0.014 mg/kg-bw/day; see Section 5.6);

SAF = soil allocation factor (0.25; see Section 8.1.1 below);

BW = body weight (16.5 kg: toddler (agricultural, residential/parkland and commercial land uses); 70.7 kg: adult (industrial land use); AENV, 2009);

AF_G = absorption (bioavailability) factor for gut (conservatively assumed to be 1.0; see Section 5.5);

SIR = soil ingestion rate (0.00008 kg/day: toddler (agricultural, residential/parkland and commercial land uses); 0.00002 kg/day: adult (industrial land use); AENV, 2009);

AF_L = absorption (bioavailability) factor for lung (conservatively assumed to be 1.0);

IR_S = inhalation of particulate matter re-suspended from soil (7.1×10^{-9} kg/day: toddler (agricultural, residential/parkland and commercial land uses); 1.2×10^{-8} kg/day: adult (industrial land use); AENV, 2009);

AF_S = absorption factor for skin (dimensionless) (0 for barite-barium based on the low likelihood of exposure via this pathway because of the low solubility of barite);

SR = adult or toddler soil dermal contact rate (kg/day; see AENV, 2009);

ET_1 = exposure term 1 (dimensionless) (1.0: agricultural and residential/parkland land uses; 0.6593: commercial and industrial land uses; AENV, 2009);

ET_2 = exposure term 2 (dimensionless) (1.0: agricultural and residential/parkland land uses; 0.4167: commercial and industrial land uses; AENV, 2009); and,

BSC = background soil concentration (325 mg/kg; see Section 2.4.3).

Substituting the appropriate values for each land use in the above equation, and rounding to 1.5 significant figures, yields values of 10,000 mg/kg (agricultural and residential/parkland), 15,000 (commercial), and 250,000 mg/kg (industrial). These values are the soil remediation guidelines for the human soil ingestion pathway (Table 6).

8.1.1 Soil Allocation Factor

AENV (2009) indicates that humans are potentially exposed to environmental contaminants through one or more of 5 media: soil, water, air, food, and consumer products. Accordingly, by default, a soil allocation factor (SAF) of 0.2 is used in calculating generic guidelines for human health pathways to ensure that the total exposure from all media does not exceed acceptable limits. However, AENV (2009) allows the SAF to be calculated by only considering environmental media through which significant exposure is likely to occur.

In the case of barium, significant exposure through air is unlikely. Health Canada (1990) states that "at the levels of barium measured in U.S. air, intake of barium through inhalation would be negligible compared with the amount ingested." This leaves four environmental

media through which exposure is considered possible, and accordingly an SAF of 0.25 was used in this project.

8.2 Inhalation of Indoor Air Check

Barite is non-volatile, and accordingly this check is not relevant and is not calculated.

8.3 Off-Site Migration Check

The off-site migration check for human health endpoints is calculated to ensure that wind and water erosion of contaminated material from a commercial or industrial site could not cause unacceptable contaminant concentrations on an adjacent property with a more sensitive land use. The check is calculated using the equation provided in AENV (2009):

$$SQG_{OM} = (14.3 \times SQG_A) - (13.3 \times BSC)$$

Where SQG_{OM}= soil remediation guideline protective of offsite migration (mg/kg);

SQG_A = soil remediation guideline for human receptors for agricultural land use (10,000 mg/kg, Table 6); and,

BSC = background soil concentration (325 mg/kg, Section 2.4.3).

Substituting these values in the above equation, and rounding to 2 significant figures, yields a value of 140,000 mg/kg, which is the ecological off-site migration check (Table 6).

8.4 Groundwater Check (Drinking Water)

This check was not calculated because it is not applicable to metals (CCME, 1999 and updates).

8.5 Produce, Meat and Milk Check

This check applies only to non-polar organic compounds, and is not calculated for metal contaminants (CCME, 1999 and updates).

8.6 Data Gaps

The major data gap in the derivation of the soil remediation guideline for barite is the lack of a high quality, sub-chronic or, preferably, chronic toxicological study of the effects of barite on a mammalian laboratory test species (*e.g.*, rat). In the absence of such a study, it was necessary to make the (likely conservative) assumptions that the tolerable daily intake

(reference dose) developed by the US EPA for soluble barium compounds was applicable to barite, and that the bioavailability of barite-barium was 100%.

9. APPLICATION OF BARITE SOIL REMEDIATION GUIDELINES

9.1 Analytical Definitions

In order to apply the soil remediation guidelines for barite correctly, it is necessary to understand two analytical definitions.

9.1.1 Extractable Barium

In this document, "extractable barium" refers to the results of soils analyses conducted using the method described in Section 6.2.2. Extractable barium is the barium that is present in soil pore water plus the barium that is sorbed to clay surfaces. Extractable barium has been shown to correlate with the barium that is bioavailable to plants and soil invertebrates.

9.1.2 Non-Barite Barium

Non-barite barium refers to barium that is not in the form of $BaSO_4$. Barium is classified as non-barite barium if extractable barium concentrations exceed the guidelines in Table 6. Non-barite barium is measured by the strong acid digest techniques described in Section 2.2.1, or may also be measured by fusion-XRF or fusion-ICP.

9.1.3 True Total Barium

In this document, "true total barium" refers to the barium results of soils analyses conducted using fusion-XRF or fusion-ICP methods. The guidelines for Barite Sites (see below) are expressed in terms of true total barium concentrations.

9.2 Guideline Application (Figure 1)

At sites where barium contamination is suspected, the assessor may first measure non-barite barium by strong acid digest and compare to the Alberta Tier 1 guideline (AENV, 2009) for barium at non-barite sites (Row C of Table 6). Since these are the most stringent guideline values, no further action will be necessary if soil barium concentrations fall below the applicable Tier 1 guideline.

Where the assessor suspects or has confirmed that barium concentrations in soil exceed the Alberta Tier 1 guideline for barium at non-barite sites (AENV, 2009), the following procedure should be used. This procedure is based on using the guideline for extractable barium to determine whether the Alberta barite guidelines can be used at a particular site. The steps for applying the barite soil remediation guidelines are as follows:

1. During initial site investigation, if barite contamination is suspected, sufficient samples should be analyzed for extractable barium to allow a determination of whether or not extractable barium at the site exceeds the applicable guideline in Row A of Table 6.
2. If all extractable barium samples are below the applicable guideline, then the site is deemed to be a "Barite Site" and the guidelines in Row B of Table 6 can be applied to true total barium concentrations at the site.
3. If all extractable barium samples exceed the applicable guideline in Row A of Table 6, then the site is not a "Barite Site" and the guidelines in Row B of Table 6 cannot be applied to total barium concentrations at the site. Instead, a proponent must either use the Tier 1 guidelines for non-barite barium (Row C in Table 6) to assess the contamination, or conduct a site-specific risk assessment.

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TABLES

Table 1. Physical and Chemical Properties of Barite

Property	*Value*	*Units*	*Source*
CAS number	7727-43-7	na	ChemFinder (2003)
Molecular formula	$BaSO_4$	na	CEPA (2002)
Physical State	crystals or powder	na	CEPA (2002)
Molecular weight	233.3876	g	ChemFinder (2003)
Hardness	3 to 3.5	Mohs scale	CRC (1983)
Specific gravity	4.2 to 4.6	na	ADMMR (2001)
Density	4.5 at 15 °C	g/cm^3	WHO (1996)
Melting point	1,580	°C	ChemFinder (2003); US EPA (2005a)
Boiling point	1,149	°C	US EPA (2005a)
Vapour pressure	"no data"	na	US EPA (2005a)
Solubility Product Constant (K_{sp} at 25 °C)	1.1×10^{-10}	na	CRC (1983)
Water solubility	1.15 at 0 °C	mg/L	US EPA (2005a)
Water solubility	2 at 18 °C	mg/L	HSDB (2005) cited in CEPA (2002)
Water solubility	2.4 at 25 °C	mg/L	US EPA (1997)
Water solubility	2.85 at 30 °C	mg/L	WHO (1996)
Organic solvent solubility	insoluble	mg/L	CEPA (2002)

Notes:
na = not applicable

Table 2. Selected Plant Toxicological Data for Barite

Organism	*Effect (% decrease)*	*Endpoint*	*Concentration (mg barite / kg dry soil)*	*Soil pH*	*Test Substrate*	*Reference*
Alsike Clover	**Emergence (32%)**	LOEC	1,000,000	8.3 – 9.1	Clay loam; 1.2% organic matter	ESG (2003a)
(*Trifolium hybridum*)	**Shoot length (20%)**	LOEC	1,000,000	8.3 – 9.1		
	Shoot wet mass	NOEC	1,000,000	8.3 – 9.1		
	Shoot dry mass	NOEC	1,000,000	8.3 – 9.1		
	Root length	NOEC	1,000,000	8.3 – 9.1		
	Root wet mass	NOEC	1,000,000	8.3 – 9.1		
	Root dry mass	NOEC	1,000,000	8.3 – 9.1		
	Nodule abundance	NOEC	1,000,000	8.3 – 9.1		
Orchardgrass	Emergence	NOEC	1,000,000	8.3 – 8.6	Clay loam; 1.2% organic matter	ESG (2003a)
(*Dactylis glomerata*)	Shoot length	NOEC	1,000,000	8.3 – 8.6		
	Shoot wet mass	NOEC	1,000,000	8.3 – 8.6		
	Shoot dry mass	NOEC	1,000,000	8.3 – 8.6		
	Root wet mass	NOEC	1,000,000	8.3 – 8.6		
	Root dry mass	NOEC	1,000,000	8.3 – 8.6		
	Nodule abundance	NOEC	1,000,000	8.3 – 8.6		
	Root length	IC20	850,000	8.3 – 8.6		

Table 2. Selected Plant Toxicological Data for Barite (Cont.)

Organism	*Effect (% decrease)*	*Endpoint*	*Concentration (mg barite / kg dry soil)*	*Soil pH*	*Test Substrate*	*Reference*
Perennial ryegrass (*Lolium perenne*)	Emergence	NOEC	1,000,000	8.3 – 8.7	Clay loam; 1.2% organic matter	ESG (2003a)
	Shoot length	NOEC	1,000,000	8.3 – 8.7		
	Shoot wet mass	NOEC	1,000,000	8.3 – 8.7		
	Shoot dry mass	NOEC	1,000,000	8.3 – 8.7		
	Root wet mass	NOEC	1,000,000	8.3 – 8.7		
	Root dry mass	NOEC	1,000,000	8.3 – 8.7		
	Nodule abundance	NOEC	1,000,000	8.3 – 8.7		
	Root length (23%)	LOEC	1,000,000	8.3 – 8.7		
	Root length	IC20	960,000	8.3 – 8.7		
Green beans (*Phaseolus vulgaris* L., 'Tendergreen')	Plant dry mass	NOEC	227,500	6.2	Dagor silt loam; 8.1% organic matter	Miller *et al.* (1980)
	Plant dry mass	NOEC	795,300	6.2		
Sweet corn (*Zea mays* var. saccharata (Sturtev.) 'Bailey' Northrup King 199)	Plant dry mass	NOEC	227,500	6.2	Dagor silt loam; 8.1% organic matter	Miller *et al.* (1980)
	Plant dry mass (20%)	LOEC	795,300	6.2		

Table 3. Selected Invertebrate Toxicological Data for Barite

Organism	*Effect*	*Endpoint*	*Concentration (mg barite / kg dry soil)*	*Soil pH*	*Test Substrate*	*Reference*
Earthworm (*Eisenia fetida*)	Survival	NOEC	17,000	5.0	Artificial soil, 11% clay, 18% silt, 71% sand: 1.2% organic matter	Simini *et al.* (2002)
Enchytraeid worm (*Enchytraeus crypticus*)	Survival	NOEC	17,000	5.0	Artificial soil; 1.2% organic matter	Kuperman *et al.* (2002)
Earthworm (*Eisenia andrei*)	Survival	NOEC	1,000,000	8.4 – 8.5	Clay loam; 1.2% organic matter	ESG (2003a)
Springtail (*Onychiurus folsomi*)	Survival	NOEC	1,000,000	8.2 – 8.4	Clay loam; 1.2% organic matter	ESG (2003a)

Table 4. Acute Barite Toxicological Data for Mammals

Organism	*Effect*	*Endpoint*	*One Time Dose (mg/kg body weight)*	*Exposure Period*	*Exposure Route*	*Reference*
CBL-Wistar	Mortality	NOEL	160,000	Acute – 1 time	Intragastric cannula	Boyd and Abel (1966)
albino rats	Mortality (from stomach rupture)	LD_{50}	307,000	Acute – 1 time	Intragastric cannula	
	Mortality (from bowel obstruction)	LD_{0}	163,000	Acute – 1 time	Intragastric cannula	
	Mortality (from bowel obstruction)	LD_{50}	364,000	Acute – 1 time	Intragastric cannula	
	Mortality (from bowel obstruction)	LD_{100}	564,000	Acute – 1 time	Intragastric cannula	

Table 5. Chronic Barite Toxicological Data for Mammals

Notes:

Organism	*Effect*	*Endpoint*	*Exposure Concentrations (mg/kg food)*	*Exposure Period*	*Exposure Route*	*Estimated Dose (mg/kg bw per day)*	*Reference*
CF-1 mice	General appearance	NOEL	8 (maximum concentration)	3 generations	oral	1.067 [1]	Hutcheson *et al.* (1975) [2]
	Morbidity and mortality	NOEL	8 (maximum concentration)	3 generations	oral	1.067 [1]	
	Abnormalities at necropsy	NOEL	0.8 (maximum concentration)	3 generations	oral	0.107 [1]	
	Weight gain	NOEL	8 (maximum concentration)	3 generations	oral	1.067 [1]	
	Reproduction and lactation (number of females having litters, average litter size, average weanling weight)	NOEL	8 (maximum concentration)	3 generations	oral	1.067 [1]	
	Hematology and serum protein levels	NOEL	0.8 (maximum concentration)	3 generations	oral	0.107 [1]	

1. *Calculated from food concentration using a value of 0.03 kg for body mass (Health Canada, 1994) and an ingestion rate of 4 g/day (Health Canada, 1994).*
2. *Hutcheson et al. (1975) fed mice food containing barite and oxides of scandium, chromium, lanthanum, samarium, europium, terbium, dysprosium, thulium, and ytterbium.*

Table 6. Soil Remediation Guidelines for Barite

THE PROCEDURE FOR APPLYING SOIL REMEDIATION GUIDELINES FOR BARITE IS FOUND IN SECTION 9.2 and FIGURE 1.

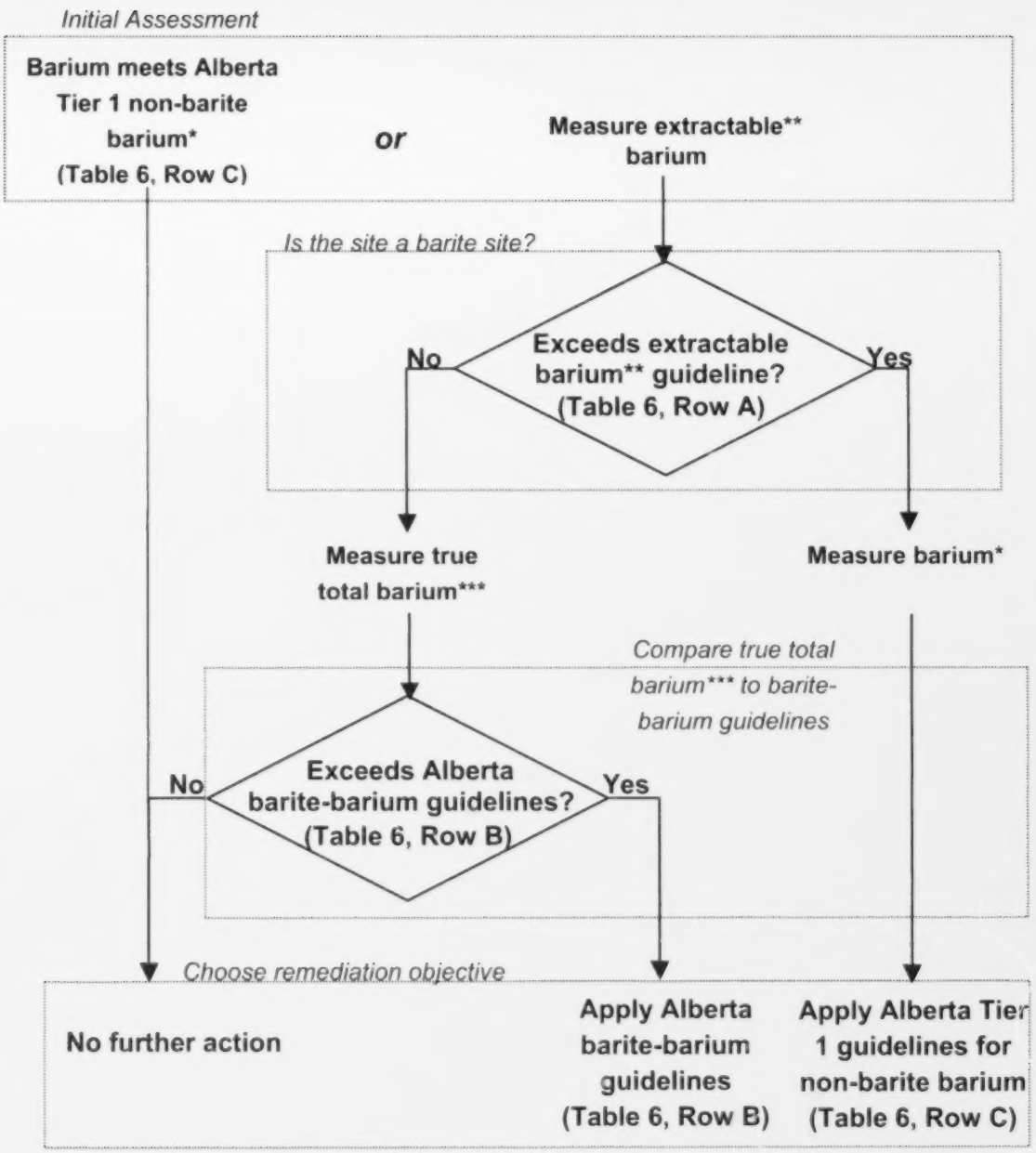
	LAND USE				
	Natural Area	*Agricultural*	*Residential/ Parkland*	*Commercial*	*Industrial*
	(mg/kg)	*(mg/kg)*	*(mg/kg)*	*(mg/kg)*	*(mg/kg)*
A: Guideline for Extractable Barium	***250***	***250***	***250***	***450***	***450***
B: Guideline for True Total Barium at Barite Sites	***10,000***	***10,000***	***10,000***	***15,000***	***140,000***
Human Health					
SQG_{HH}	---	10,000	10,000	15,000	250,000
Soil ingestion guideline	---	10,000	10,000	15,000	250,000
Inhalation of indoor air check	---	NC [a]	NC [a]	NC [a]	NC [a]
Off-Site migration check	---	---	---	140,000	140,000
Groundwater check (drinking water)	NC [b]	NC [b]	NC [b]	NC [b]	NC [b]
Produce, meat, and milk check	---	NC [c]	NC [c]	NC [c]	NC [c]
Environment					
SQG_E	10,000	10,000	200,000	140,000	140,000
Soil contact guideline	200,000	200,000	200,000	200,000	200,000
Livestock soil ingestion guideline	30,000	30,000	---	---	---
Wildlife soil ingestion guideline	10,000	10,000	---	---	---
Nutrient and energy cycling check	NC [d]	NC [d]	NC [d]	NC [d]	NC [d]
Off-site migration check	---	---	---	140,000	140,000
Groundwater check (aquatic life)	NC [b]	NC [b]	NC [b]	NC [b]	NC [b]
C: Alberta Tier 1 Guideline for Barium at Non-Barite Sites	**750**	**750**	**500**	**2,000**	**2,000**

Notes:
--- = guideline/check value is not part of the exposure scenario for this land use and therefore is not calculated.
NC = not calculated.
NA = not applicable: pathway not part of the exposure scenario for this land use or calculated guideline value exceeds 1,000,000 mg/kg.

a. This guideline is not calculated because barite is non-volatile.
b. Applies to organic compounds and is not calculated for metal contaminants.
c. The produce, milk and meat check applies to organic contaminants and is thus not calculated for inorganic contaminants.
d. Data are insufficient/inadequate to calculate these guidelines/check values.

NOTE: THESE GUIDELINES MAY ONLY BE USED WHEN BARIUM CONCENTRATIONS ARE MEASURED USING A TRUE TOTAL BARIUM TECHNIQUE – SEE SECTION 9.1.2

Figure 1. Guideline Application Procedure


Initial Assessment
Barium meets Alberta Tier 1 non-barite barium* (Table 6, Row C)
or
Measure extractable** barium
Is the site a barite site?
Exceeds extractable barium** guideline? (Table 6, Row A)
No
Yes
Measure true total barium***
Measure barium*
Compare true total barium*** to barite-barium guidelines
Exceeds Alberta barite-barium guidelines? (Table 6, Row B)
No
Yes
Choose remediation objective
No further action
Apply Alberta barite-barium guidelines (Table 6, Row B)
Apply Alberta Tier 1 guidelines for non-barite barium (Table 6, Row C)

* - Barium is measured in a strong acid digest or by fusion-XRF or fusion-ICP for comparison to non-barite barium guidelines.

** - Extractable barium is measured in a 0.1M $CaCl_2$ extract.

*** - True total barium must be measured by fusion-XRF or fusion-ICP methods.